Ru-Based *Z*-Selective Metathesis Catalysts with Modified Cyclometalated Carbene Ligands

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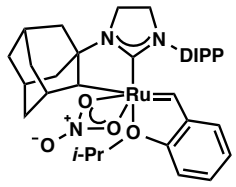
Materials and Methods. All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ and C_6D_6 were used as received. All substrates for olefin cross-metathesis (**29**, **32**, **34**, **36**, **37**, **39**, and **40**) were degassed with argon and filtered through a plug of neutral alumina prior to use. $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (**3**) was obtained from Materia, Inc. Other commercially available reagents and silica gel were used as received. **7**[1] and **8**[2] were obtained from Materia and were prepared according to standard literature procedures. CAACs were obtained from the Bertrand laboratory. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV and potassium permanganate staining. EMD silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Varian spectrometers (at 300 MHz or 500 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Spectrometers (at 125 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift, and when necessary, multiplicity, and coupling constant (Hz). High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer.

Experimental Procedures.

A. Synthesis and Characterization of Ruthenium Metathesis Catalysts



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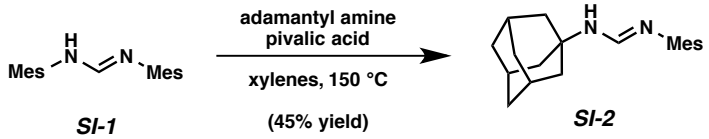
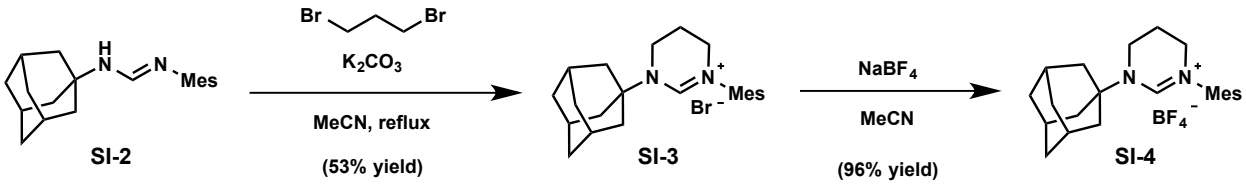
Nitrate 8. A crystal suitable for X-ray crystallography was prepared by recrystallization via slow diffusion of pentane into a solution of **8** in Et_2O.



SI-1 ***SI-2***

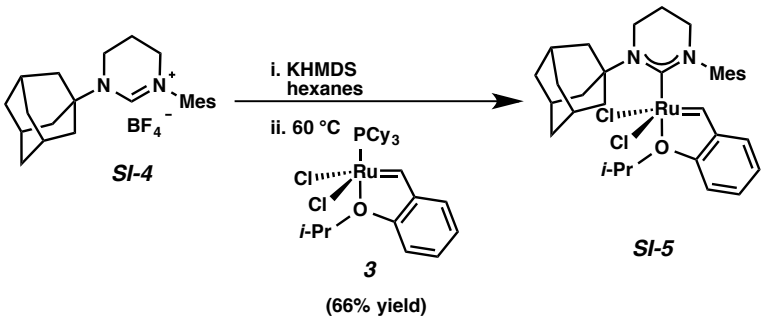
Adamantyl Mesityl Formamidine SI-2. To a round bottom flask was added bis-mesityl formamidine[3] (**SI-1**) (10.0 g, 35.7 mmol, 1.00 equiv), adamantyl amine (5.40 g, 35.7 mmol, 1.00 equiv), pivalic acid (200 mg, 1.96 mmol, 5.00 mol%), and xylenes (30 mL). The flask was affixed with a reflux condenser, and the mixture was heated to 150 °C. The solution was stirred for 4 d and then cooled to room temperature. Hexanes (60 mL) was added to the mixture, and resulting solids were removed by filtration. The filtrate was collected and then concentrated to dryness *in vacuo*. Purification by flash chromatography (30:10:1 CH_2Cl_2:Benzene:MeOH) provided adamantyl mesityl formamidine **SI-2** as a tan solid (4.79 g, 16,2 mmol, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of isomers): δ 7.43 (d, J = 12.5, 0.5 H), 7.36 (s, 0.5 H), 6.85 (s, 2H), (br d, J = 12.5, 1H), 2.26 (s, 3H), 2.16–2.08 (m, 9H), 1.84 (s, 3H), 1.72–1.60 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of isomers): δ 151.3 (N=CH–N), 144.1, 143.2, 131.5,

130.6 (N=CH–N), 128.8, 128.7, 128.5, 51.1, 50.5, 44.2, 43.8, 36.1, 36.0, 29.4, 28.3, 20.7, 18.6, 17.8; HRMS-FAB (*m/z*) $[M + H]^+$ calcd for $C_{20}H_{29}N_2$, 297.2331; found, 297.2330.

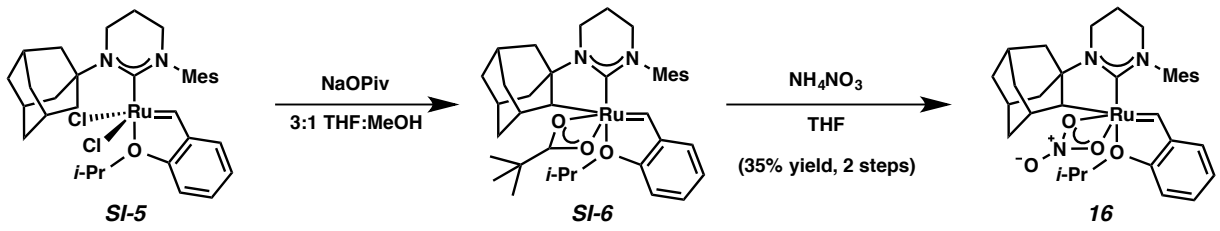


Formamidinium salt SI-4. To a solution of formamidine **SI-2** (1.00 g, 3.37 mmol, 1.00 equiv) in MeCN (70 mL) was added K_2CO_3 (233 mg, 1.69 mmol, 0.50 equiv) and 1,3-dibromopropane (0.376 mL, 3.71 mmol, 1.10 equiv). The reaction vessel was placed in a heating bath maintained at 85 °C for 16 h. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting solids were taken up in CH_2Cl_2 and passed through a fritted filter to remove K_2CO_3. The filtrate was concentrated under reduced pressure, and taken up CH_2Cl_2 (20 mL) followed by Et_2O (100 mL) and the resulting solution was placed in the freezer overnight. White solids that precipitated from solution were isolated and washed with Et_2O, then dried under reduced pressure to give **SI-3** (615 mg, 1.47 mmol, 53% yield)**.**

SI-3 (615 mg, 1.47 mmol, 1.00 equiv) was taken up in MeCN (7.0 mL), treated with $NaBF_4$ (1.61 g, 14.7 mmol, 10.0 equiv), and was stirred at 23 °C for 2 hours. The solution was filtered over celite and washed through with CH_2Cl_2. Evaporation of the solvent under reduced pressure afforded **SI-4** (600 mg, 1.41 mmol, 96% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1H), 6.96 (s, 2H), 4.10 (t, *J* = 5.6, 2H), 3.88 (t, *J* = 5.6, 2H), 2.43–2.38 (m, 2H), 2.30 (s, 9H), 2.28 (br s, 3H), 2.04 (d, *J* = 2.8, 6H), 1.75 (d, *J* = 12.7, 3H), 1.69 (d, *J* = 12.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.9, 140.2, 137.4, 134.9, 130.2, 62.1, 47.0, 40.6, 39.5, 35.5, 29.5, 21.1, 20.0, 18.4; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{23}H_{33}N_2$, 337.2644; found, 337.2650.

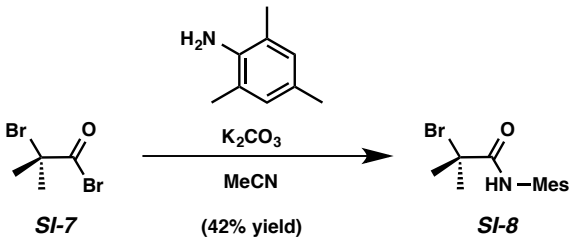


Ruthenium Dichloride SI-5. In a glovebox, a Schlenk flask containing a solution of BF_4 salt **SI-4** (300 mg, 0.710 mmol, 2.40 equiv) in hexanes (10 mL) was treated with KHMDS (133 mg, 0.670 mmol, 2.28 equiv). The mixture was allowed to stir at 23 °C for 2 h, filtered through a PTFE plug, and was then treated with **3** (177 mg, 0.290 mmol, 1.00 equiv). The vessel was sealed and after stirring for 6 h at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The precipitated solids were filtered over celite and washed with hexanes and Et_2O. Evaporation of the solvent under reduced pressure afforded **SI-5** (126 mg, 0.192 mmol, 66% yield) as a green powder. ^{1}H NMR (500 MHz, C_6D_6): δ 16.67 (s, 1H), 7.24–7.20 (m, 2H), 6.88 (s, 2H), 6.80 (t, *J* = 7.4, 1H), 6.46 (d, *J* = 8.1, 1H), 4.54 (sept, *J* = 6.2, 1H), 3.13–3.05 (m, 9H), 2.41 (s, 6H), 2.32 (br s, 3H), 2.27 (s, 3H), 1.88 (d, *J* = 11.9, 3H), 1.69 (d, *J* = 12.2, 3H), 1.49 (d, *J* = 6.2, 9H); ^{13}C NMR (125 MHz, C_6D_6, 29/30 C): δ 214.3, 152.5, 147.4, 146.1, 137.7, 131.3, 130.4, 130.0, 127.0, 123.3, 122.4, 120.6, 113.6, 74.5, 69.9, 62.1, 52.6, 42.2, 41.0, 36.6, 30.6, 29.9, 27.9, 22.7, 22.5, 22.3, 21.0, 19.6, 16.7; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{33}H_{44}ORuN_2Cl_2$, 656.1875; found, 656.1907.



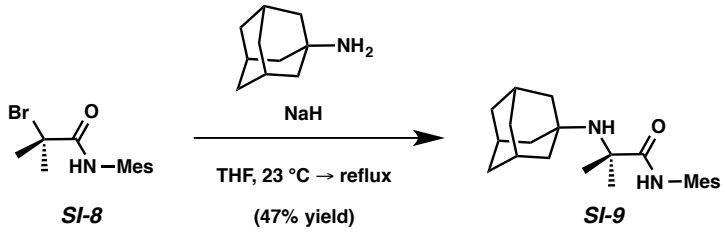
Nitrate 16. In a glovebox, a 20 mL vial containing a solution of **SI-5** (50.0 mg, 0.0761 mmol, 1.00 equiv) in 3:1 THF:MeOH (5 mL) was treated with NaOPiv (94.0 mg, 0.761 mmol, 10.0

equiv). After stirring for 1 h at 23 °C in the glove box, the purple mixture was concentrated under reduced pressure, then taken up in THF (5 mL) and filtered through celite. The filtrate was treated with NH_4NO_3 (182 mg, 2.30 mmol, 30.0 equiv) and allowed to stir for 1 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated and triturated with Et_2O until the washes became colorless providing **16** as a purple solid (17.0 mg, 0.0263 mmol, 35 % yield, 2 steps). ^{1}H NMR (500 MHz, C_6D_6): δ 15.53 (s, 1H), 7.49 (dd, *J* = 7.5, 1.6, 1H), 7.21 (ddd, *J* = 8.7, 7.5, 1.6, 1H), 7.07 (s, 1H), 6.86 (td, *J* = 7.8, 0.5, 1H), 6.64 (s, 1H), 6.45 (d, *J* = 8.4, 1H), 4.47 (sept, *J* = 6.3, 1H), 4.36 (s, 1H), 2.96–2.85 (m, 1H), 2.81–2.76 (m, 1H), 2.69 (ddd, *J* = 13.2, 7.1, 3.8, 2H), 2.45 (s, 3H), 2.30 (s, 3H), 2.19 (s, 3H), 2.11–2.08 (m, 1H), 2.01–1.99 (m, 1H), 1.88 (m, 2H), 1.80–1.73 (m, 2H), 1.60–1.58 (m, 1H), 1.51–1.47 (m, 1H), 1.44–1.40 (m, 2H), 1.36 (d, *J* = 6.4, 3H), 1.26–1.22 (m, 2H), 1.09–1.04 (m, 1H), 1.00–0.97 (m, 1H), 0.95 (d, *J* = 6.2, 3H), 0.59 (br d, 1H); ^{13}C NMR (125 MHz, C_6D_6): δ 263.9, 206.9, 154.6, 144.0, 142.2, 136.8, 136.4, 133.6, 130.6, 130.1, 126.5, 123.34, 123.29, 113.6, 74.2, 69.4, 66.7, 49.3, 43.7, 40.2, 38.7, 38.2, 38.0, 36.5, 33.1, 31.2, 30.0, 23.2, 21.2, 21.1, 20.3, 18.2, 18.1; HRMS-FAB (*m/z*) $[M + H]^+$ calcd for $C_{33}H_{44}RuN_3O_4$, 648.2376; found, 648.2355.

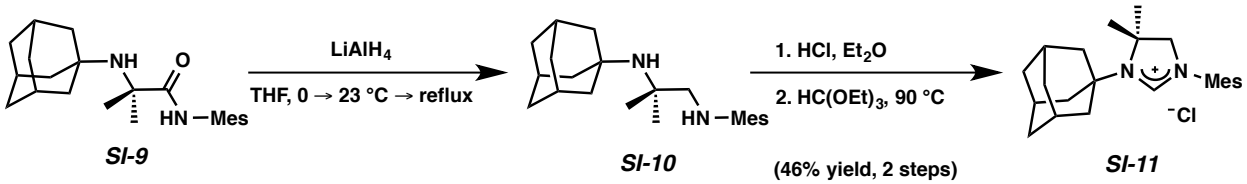


α-Bromo Mesitylamide SI-8. Following the procedure of Chung *et. al.*,[4] a solution of α-bromoisobutyryl bromide (**SI-7)** (8.33 mL, 66.5 mmol, 1.00 equiv) in MeCN (200 mL) was treated with K_2CO_3 (18.4 g, 133 mmol, 2.00 equiv). 2,4,6-Trimethylaniline (9.30 mL, 66.5 mmol, 1.00 equiv) was added and the reaction was allowed to stir for 16 h. Solids were then removed by filtration, and the filtrate was concentrated under reduced pressure. The resulting solid was dissolved in minimal CH_2Cl_2 and hexanes were added to the concentrated solution. The

resulting precipitate was isolated and washed with hexanes to provide α-bromo mesitylamide **SI-8** (7.90 g, 27.8 mmol, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 6.91 (s, 2H), 2.29 (s, 3H), 2.20 (s, 6H), 2.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 137.3, 135.2, 130.9, 129.1, 63.2, 32.8, 21.1, 18.2; HRMS-FAB (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{19}NOBr$, 284.0650; found, 284.0641.

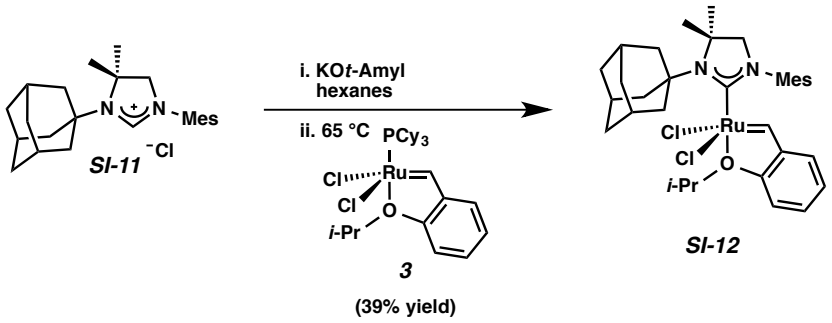


α-Amino Mesitylamide SI-9. To a solution of α-bromo mesitylamide **SI-8** (6.3 g, 22 mmol, 1.0 equiv) in THF (200 mL) was added 60% NaH (1.8 g, 44 mmol, 2.0 equiv) followed by adamantyl amine (4.0 g, 27 mmol, 1.2 equiv). The mixture stirred for 4 d at 23 °C, and was then placed in a heating bath maintained at 100 °C and allowed to stir at reflux for an additional 24 h, then diluted with saturated aqueous NH_4Cl (100 mL). The volatiles were removed under reduced pressure, and the aqueous solution was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Further purified by flash chromatography (5:1 Hexanes:EtOAc) provided **SI-9** (3.7 g, 10 mmol, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 33/34 H): δ 9.09 (s, 1H), 6.89 (s, 2H), 2.27 (s, 3H), 2.22 (s, 6H), 2.06 (br s, 3H), 1.85 (s, 3H), 1.84 (s, 3H), 1.66 (d, *J* = 12.3, 3H), 1.61 (d, *J* = 12.1, 3H), 1.55 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.9, 136.1, 134.6, 132.1, 129.1, 59.4, 52.7, 45.2, 36.6, 29.9, 29.7, 20.9, 19.1; HRMS-FAB (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{35}N_2O$, 355.2749; found, 355.2762.

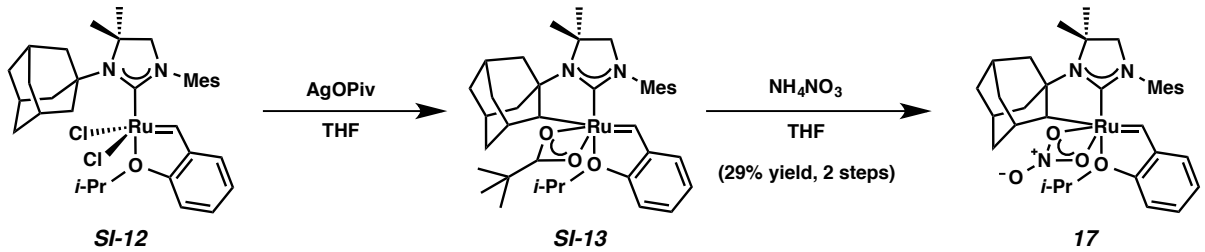


Formamidinium salt SI-11. To a solution of α-amino mesitylamide **SI-9** (1.1 g, 3.1 mmol, 1.0 equiv) at 0 °C in THF (40 mL) was added $LiAlH_4$ (0.47 g, 12 mmol, 4.0 equiv). The reaction mixture was warmed to 23 °C and then placed in a heating bath maintained at 65 °C for 9 d. The solution was cooled 0 °C and quenched with H_2O (1 mL) and 15% aqueous NaOH (1 mL). The biphasic mixture was further diluted with H_2O (20 mL) and EtOAc (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried over Na_2SO_4. Evaporation under reduced pressure afforded crude diamine **SI-10** (0.897 g, 2.64 mmol) as a yellow oil, which was used in the subsequent step without further purification.

Crude diamine **SI-10** was dissolved in Et_2O (20 mL) and treated with HCl (2.0 M in dioxane, 2.77 mL, 5.53 mmol, 2.1 equiv). The resulting white precipitate was isolated and washed with Et_2O, and then dried under reduced pressure to provide the HCl salt as white powder. The HCl salt of **SI-10** was treated with triethylorthoformate (9.0 mL, 54 mmol, 20 equiv). The reaction vessel was placed in a heating bath maintained at 90 °C for 3 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting solid was washed with hexanes to provide formamidinium salt **SI-11** (0.465 g, 1.20 mmol, 46% yield, 2 steps) as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 6.92 (s, 2H), 3.80 (s, 2H), 2.36–2.24 (m, 18H), 1.86–1.71 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 140.1, 135.2, 130.9, 130.2, 68.9, 66.0, 62.9, 43.4, 35.4, 30.0, 29.5, 21.2, 18.4; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{24}H_{35}N_2$, 351.2800; found, 351.2787.

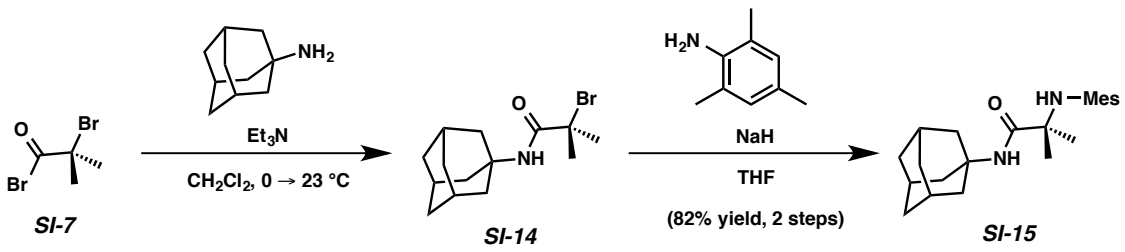


Ruthenium Dichloride SI-12. In a glove box, a Schlenk flask containing a solution of formamidinium salt **SI-11** (370 mg, 0.96 mmol, 1.05 equiv) in hexanes (25 mL) was treated with KCO_2Me_2Et (126 mg, 1.0 mmol, 1.1 equiv). The mixture was allowed to stir at 23 °C for 2 h, and was then treated with **3** (547 mg, 0.91 mmol, 1.0 equiv). After stirring for 6.5 h at 65 °C outside the glove box, the flask was cooled to room temperature. The precipitated solids were filtered and washed with hexanes. Further purification by flash chromatography (1:1:1 Pentane:Et_2O:CH_2Cl_2 → 100% CH_2Cl_2) provided ruthenium dichloride **SI-12** (0.240 g, 0.358 mmol, 39% yield) as a green powder. ^{1}H NMR (400 MHz, C_6D_6): δ 17.25 (s, 1H), 7.21 (t, *J* = 7.6, 1H), 7.16–7.14 (m, 1H), 6.85 (s, 2H), 6.75 (t, *J* = 7.4, 1H), 6.47 (d, *J* = 8.4, 1H), 4.56 (sept, *J* = 5.7, 1H), 3.26 (br s, 6H), 3.07 (s, 2H), 2.40 (s, 6H), 2.34 (br s, 3H), 2.25 (s, 3H), 1.96 (d, *J* = 12.0, 3H), 1.69 (d, *J* = 12.4, 3H), 1.52 (d, *J* = 6.0, 6H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 22/23 C): δ 210.8, 152.8, 146.9, 140.5, 138.4, 138.2, 130.2, 130.0, 123.5, 122.5, 113.5, 74.4, 68.5, 64.3, 60.4, 43.1, 36.3, 31.0, 30.2, 22.6, 21.1, 18.8; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{34}H_{46}Cl_2N_2ORu$, 670.2031; found, 670.2059.



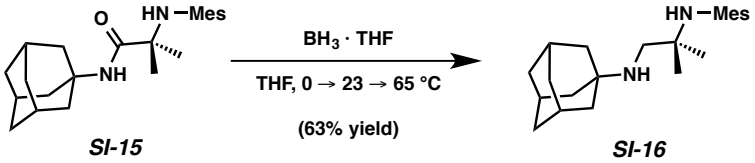
Nitrate 17. In a glovebox, a Schlenk flask containing a solution of **SI-12** (20 mg, 0.030 mmol, 1.0 equiv) in THF (1.0 mL) was treated with AgOPiv (20 mg, 0.090 mmol, 3.0 equiv). After stirring for 30 min and a color change from brown to purple was observed, the mixture was filtered through celite and concentrated under reduced pressure. The residue was triturated with Et_2O and dried to provide crude **SI-13** as a purple solid, which was used without further purification.

Crude **SI-13** was dissolved in THF (3.0 mL), treated with NH_4NO_3 (72 mg, 0.90 mmol, 30 equiv) and allowed to stir for 1 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated and triturated with Et_2O until the washes became colorless providing **17** as a purple solid (5.9 mg, 0.0076 mmol, 29 % yield, 2 steps). ^{1}H NMR (400 MHz, C_6D_6): δ 15.29 (s, 1H), 7.43 (d, *J* = 7.0, 1H), 7.20 (t, *J* = 7.2, 1H), 7.01 (s, 1H), 6.84 (t, *J* = 7.4, 1H), 6.65 (s, 1H), 6.49 (d, *J* = 8.3, 1H), 4.55 (sept, *J* = 6.5, 1H), 4.16 (s, 1H), 3.29 (d, *J* = 10.1, 1H), 3.11 (d, *J* = 10.0, 1H), 2.48 (s, 3H), 2.41 (s, 3H), 2.27–2.24 (m, 3H), 2.12 (s, 3H), 2.09 (d, *J* = 6.6, 2H), 2.00 (d, *J* = 11.8, 1H), 1.76 (d, *J* = 11.6, 1H), 1.70 (d, *J* = 11.9, 1H), 1.60 (br s, 1H), 1.53–1.46 (m, 2H), 1.39 (d, *J* = 6.3, 3H), 1.22 (d, *J* = 13.4, 6H), 1.03 (br d, *J* = 12.0, 1H), 0.96 (d, *J* = 6.2, 3H), 0.61 (br d, *J* = 12.3, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 265.4, 211.8, 154.6, 143.8, 137.6, 137.3, 136.1, 135.5, 130.1, 129.6, 126.8, 123.5, 123.4, 113.1, 74.2, 68.4, 67.6, 66.6, 62.1, 44.9, 41.8, 40.2, 38.22, 38.15, 32.6, 32.3, 30.4, 30.3, 28.9, 21.2, 21.1, 20.2, 18.6, 18.0; HRMS-FAB (*m/z*) $[(M + H)–H_2]^+$ calcd for $C_{34}H_{44}N_3O_4Ru$, 660.2376; found, 660.2382.



α-Amino Adamantylamide SI-15. Following the procedure of Chung *et. al.*,[4] a solution of α-bromoisobutyryl bromide (**SI-7**) (1.35 mL, 11.0 mmol, 1.10 equiv) in CH_2Cl_2 (20 mL) at 0 °C was treated with Et_3N (2.80 g, 20.0 mmol, 2.0 equiv). 1-Adamantylamine (1.51 g, 10.0 mmol, 1.00 equiv) was added in four portions, and the reaction mixture was warmed to 25 °C and stirred for 3 h. The reaction mixture was then diluted with CH_2Cl_2 (30 mL) and washed with saturated aqueous NH_4Cl (2 x 20 mL). The organic layer was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded crude **SI-14** as an off-white solid, which was used in the subsequent step without further purification.

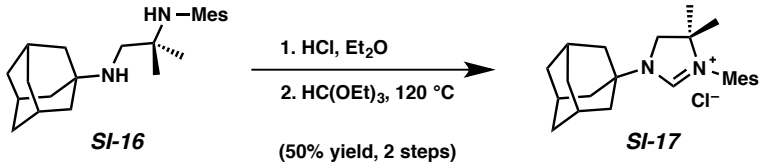
Crude **SI-14** was dissolved in THF (25 mL) and added dropwise to solution of NaH (0.480 g, 20 mmol, 2.00 equiv) and 2,4,6-trimethylaniline (1.68 mL, 12 mmol, 1.20 equiv) in THF (25 mL). The reaction mixture was allowed to stir for 16 h and was then diluted with saturated aqueous NH_4Cl (20 mL) and extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Further purification by flash chromatography (96:4 CH_2Cl_2:MeOH) provided **SI-15** (2.9 g, 8.2 mmol, 82% yield) as a white powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (br s, 1H), 6.82 (s, 2H), 3.06 (s, 1H), 2.24–2.22 (m, 9H), 2.11–2.05 (m, 9H), 1.72–1.70 (m, 6H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 140.6, 132.9, 132.3, 129.7, 60.1, 51.1, 41.5, 36.6, 29.6, 27.3, 20.7, 20.5; HRMS-FAB (*m/z*) [M + H]$^+$ calcd for $C_{23}H_{35}N_2O$, 355.2749; found, 355.2751.



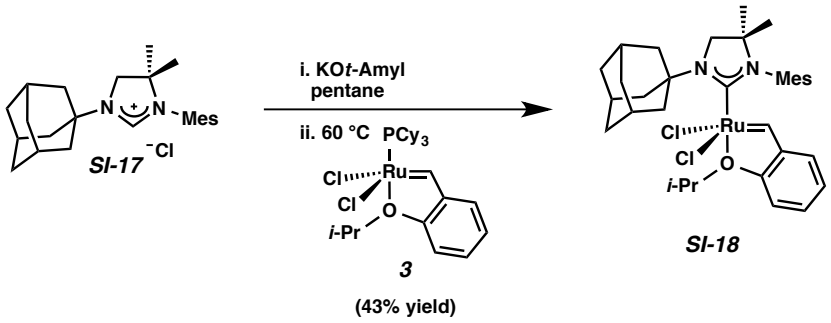
SI-15 *SI-16*

Diamine SI-16. To a solution of amine **SI-15** (1.2 g, 3.4 mmol, 1.0 equiv) in THF (5 mL) at 0 °C was slowly added BH_3 · THF (1 M in THF, 13.6 mL, 13.6 mmol, 4.0 equiv). The reaction mixture was warmed to 23 °C and then placed in a heating bath maintained at 65 °C for 2 h. After cooling to 0 °C, the reaction mixture was quenched with the dropwise addition of MeOH. The mixture was warmed to 23 °C and concentrated under reduced pressure. MeOH was added

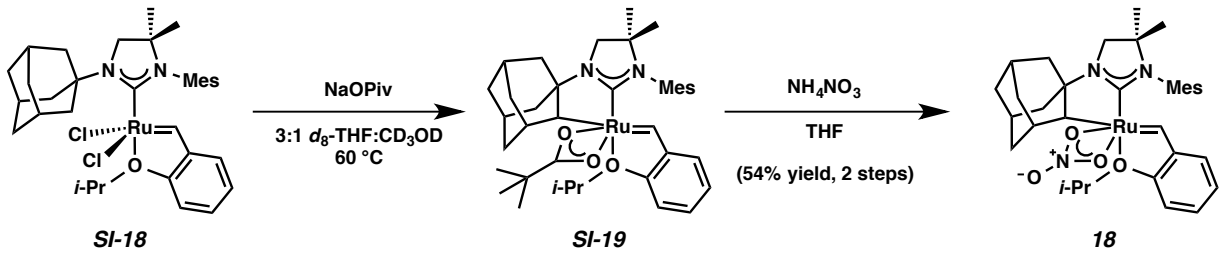
to the residue, volatiles were again evaporated under reduced pressure, and this procedure was repeated three times. Further purification by flash chromatography (9:1 CH_2Cl_2:MeOH) provided diamine **SI-16** (0.750 g, 2.19 mmol, 65% yield) as an amber oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 34/36 H): δ 6.83 (s, 2H), 2.64 (s, 2H), 2.30 (s, 6H), 2.23 (s, 3H), 2.09 (br s, 3H), 1.69–1.64 (m, 12H), 1.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 134.6, 132.2, 129.3, 62.9, 56.6, 52.9, 43.2, 37.0, 29.8, 26.9, 20.8, 20.4; HRMS-FAB (*m*/*z*) $[M + H]^+$ calcd for $C_{23}H_{37}N_2$, 341.2957; found, 341.2940.



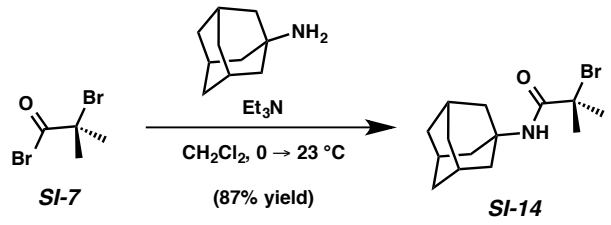
Formamidinium salt SI-17. To a solution of diamine **SI-16** (0.750 g, 2.20 mmol, 1.00 equiv) in Et_2O (10 mL) was added HCl (2.0 M in Et_2O, 4.40 mL, 8.80 mmol, 2.00 equiv). The resulting white precipitate was isolated and washed with Et_2O, and then dried under reduced pressure to provide the HCl salt as white powder. The HCl salt of **SI-16** was treated with triethylorthoformate (7.0 mL, 42 mmol, 19 equiv). The reaction vessel was placed in a heating bath maintained at 120 °C for 30 min. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting solid was washed with hexanes to provide formamidinium salt **SI-17** (0.42 g, 1.1 mmol, 50% yield, 2 steps) as a white powder. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.50 (s, 1H), 6.96 (s, 2H), 3.99 (d, J = 0.5, 2H), 2.36 (s, 6H), 2.28–2.27 (m, 6H), 2.21–2.20 (m, 6H), 1.78 (d, J = 12.8, 3H), 1.73 (d, J = 12.5, 3H), 1.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 139.8, 137.3, 130.4, 128.3, 69.7, 58.0, 57.5, 40.9, 35.5, 29.2, 26.5, 21.0, 20.0; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{24}H_{35}N_2$, 351.2800; found, 351.2809.



Ruthenium Dichloride SI-18. In a glove box, a Schlenk flask containing a solution of formamidinium salt **SI-17** (101 mg, 0.279 mmol, 1.00 equiv) in pentane (6 mL) was treated with KCO_2Me_2Et (38.7 mg, 0.307 mmol, 1.10 equiv). The mixture was allowed to stir at 35 °C for 3 h, and was then treated with **3** (168 mg, 0.279 mmol, 1.00 equiv). After stirring for 4 h at 60 °C outside the glove box, the flask was cooled to room temperature. The precipitated solids were filtered and washed with hexanes. Further purification by flash chromatography (4:1 Hexanes:Et_2O → 2:3 Hexanes:Et_2O) provided ruthenium dichloride **SI-18** (74 mg, 0.119 mmol, 43% yield) as a green powder. ^{1}H NMR (C_6D_6, 300 MHz): δ 17.08 (s, 1H), 7.21 (t, *J* = 6.6, 1H), 7.16–7.14 (m, 1H), 6.88 (s, 2H), 6.75 (t, *J* = 7.4, 1H), 6.48 (d, *J* = 8.3, 1H), 4.58 (sept, *J* = 6.2, 1H), 3.23 (s, 2H), 2.99 (br s, 6H), 2.38 (s, 6H), 2.33 (br s, 3H), 2.22 (s, 3H), 1.93 (d, *J* = 12.3, 3H), 1.76–1.70 (m, 3H), 1.57 (d, *J* = 6.0, 6H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 308.1, 210.0, 152.8, 146.5, 140.5, 138.2, 137.9, 130.3, 129.9, 123.2, 122.5, 113.6, 74.2, 65.3, 59.3, 57.1, 42.0, 36.5, 30.5, 26.5, 22.5, 21.1, 20.9; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{34}H_{46}Cl_2N_2ORu$, 670.2031; found, 670.2023.

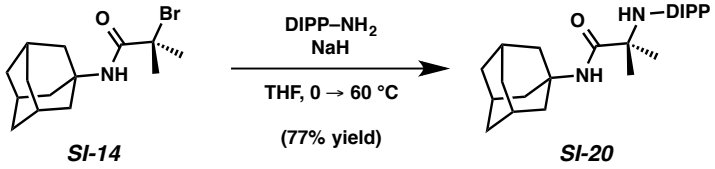


Nitrate 18. In a glovebox, a J-Young NMR tube containing a solution of **SI-18** (25.0 mg, 0.0373 mmol, 1.00 equiv) in 3:1 d_8-THF:CD_3OD (2.5 mL) was treated with NaOPiv (69.0 mg, 0.559 mmol, 15.0 equiv). After heating for 5.5 h at 60 °C outside the glove box, the tube was cooled to room temperature and transferred back to the glove box. The purple mixture was concentrated under reduced pressure, then taken up in THF (15 mL) and filtered through celite. The filtrate was concentrated, taken up in THF (2 mL) then treated with NH_4NO_3 (44.7 mg, 0.559 mmol, 15.0 equiv) and allowed to stir for 1.5 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated and triturated with Et_2O until the washes became colorless. The filtrate was dried under reduced pressure to give **18** as a violet solid (13.3 mg, 0.0201 mmol, 54% yield, 2 steps). ^{1}H NMR (400 MHz, C_6D_6): δ 15.28 (s, 1H), 7.40 (d, *J* = 7.4, 1H), 7.20 (t, *J* = 8.1, 1H), 7.00 (s, 1H), 6.83 (t, *J* = 7.4, 1H), 6.69 (s, 1H), 6.49 (d, *J* = 8.4, 1H), 4.59 (sept, *J* = 6.4, 1H), 4.23 (s, 1H), 3.18 (d, *J* = 9.8, 1H), 3.07 (d, *J* = 9.8, 1H), 2.44 (d, *J* = 8.4, 6H) 2.27 (br s, 1H), 2.13 (br s, 1H), 2.10 (s, 3H), 2.04–1.97 (m, 2H), 1.90 (br d, *J* = 11.6, 1H), 1.79 (br d, *J* = 12.0, 1H), 1.66 (br s, 1H), 1.58–1.49 (m, 2H), 1.47–1.43 (m, 4H), 1.14–1.10 (m, 2H), 1.08 (s, 3H), 1.00 (s, 3H), 0.97 (d, *J* = 6.3, 3H), 0.60 (br d, *J* = 12.2, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 265.9, 212.1, 154.7, 143.7, 139.9, 137.4, 137.0, 133.6, 130.4, 129.8, 126.7, 123.39, 123.36, 113.1, 74.3, 67.7, 66.8, 62.9, 56.2, 43.1, 40.3, 38.04, 37.96, 37.9, 33.3, 31.0, 29.9, 28.8, 26.2, 21.2, 21.0, 20.7, 20.3, 20.0; HRMS-FAB (*m/z*) $[(M + H)–H_2]^+$ calcd for $C_{34}H_{44}N_3O_4Ru$, 660.2376; found, 660.2397.



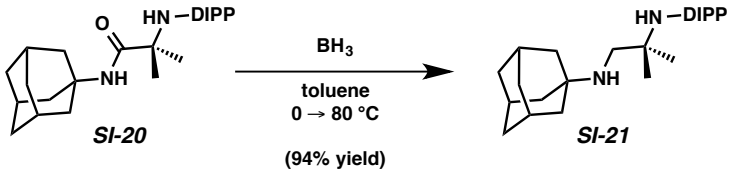
α-Bromo Adamantylamide SI-14. Following the procedure of Chung *et. al.*,[4] a solution of α-bromoisobutyryl bromide (**SI-7**) (4.05 mL, 33.0 mmol, 1.10 equiv) in CH_2Cl_2 (60 mL) at 0 °C was treated with Et_3N (8.40 mL, 60.0 mmol, 2.00 equiv). Adamantylamine (4.53 g, 30.0 mmol,

1.00 equiv) was added in three separate portions, and the reaction was warmed to 23 °C and stirred for 2 h. Additional CH_2Cl_2 (60 mL) was added to dissolve solids, and the reaction was allowed to stir for 3 h. The reaction was diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous NH_4Cl (3 × 200 mL). The organic layer was dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded **SI-14** (7.83 g, 26.1 mmol, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.44 (br s, 1H), 2.11 (br s, 3H), 2.02 (d, *J* = 3.0, 6H), 1.93 (s, 6H), 1.70 (t, *J* = 3.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 64.0, 52.4, 41.2, 36.5, 32.7, 29.5; HRMS-FAB (*m*/*z*) $[M + H]^+$ calcd for $C_{14}H_{23}NOBr$, 300.0963; found, 300.0966.

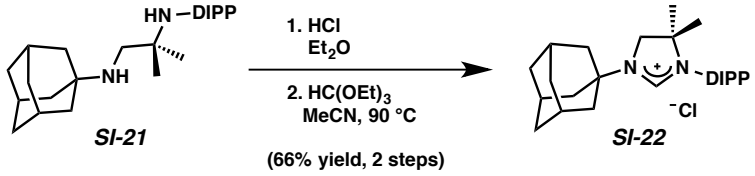


SI-14 *SI-20*

α-Amino Adamantylamide SI-20. To a solution of α-bromo adamantylamide **SI-14** (2.33 g, 7.77 mmol, 1.00 equiv) in THF (40 mL) at 0 °C was added 60% NaH (0.648 g, 15.5 mmol, 2.00 equiv) followed by 90% 2,6-diisopropylaniline (1.95 mL, 9.32 mmol, 1.20 equiv). The resulting mixture was removed from the bath and allowed to warm to 23 °C. After stirring for 2 d, additional NaH (0.610 g, 14.6 mmol, 1.88 equiv) was added to the reaction mixture, which was placed in a heating bath maintained at 60 °C. The mixture was stirred for 2 d, then cooled to 23 °C and quenched with H_2O (50 mL). The biphasic mixture was further diluted with CH_2Cl_2 (50 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried over $MgSO_4$. Evaporation under reduced pressure afforded **SI-20** (2.37 g, 5.97 mmol, 77% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 7.64 (br s, 1H), 7.08–7.06 (m, 3H), 3.23 (sept, *J* = 7.0, 2H), 3.09 (s, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 2.00 (br s, 3H), 1.66 (d, *J* = 12.5, 3H), 1.58 (d, *J* = 12.0, 3H), 1.32 (s, 6H), 1.17 (d, *J* = 6.5, 12H); ^{13}C NMR (125 MHz, C_6D_6): δ 176.0, 144.4, 139.9, 125.3, 123.8, 60.9, 50.9, 41.7, 36.8, 30.0, 28.5, 27.2, 24.2; HRMS-FAB (*m*/*z*) $[M + H]^+$ calcd for $C_{26}H_{41}N_2O$, 397.3219; found, 397.3220.

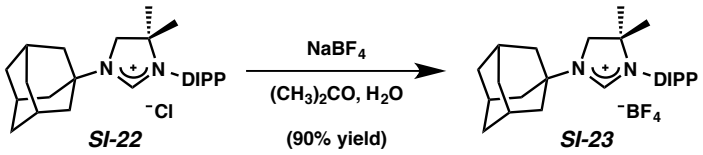


Diamine SI-21. To a solution of amine **SI-20** (7.10 g, 17.9 mmol, 1.00 equiv) in toluene (179 mL) was added $BH_3 \cdot THF$ (1 M in THF, 35.8 mL, 35.8 mmol, 2 equiv) and $BH_3 \cdot Me_2S$ (2 M in THF, 17.9 mL, 35.8 mmol, 2 equiv). The reaction mixture placed in a heating bath maintained at 80 °C for 5 d, then allowed to cool to 23 °C, and quenched with H_2O (400 mL). The biphasic mixture was further diluted with CH_2Cl_2 (400 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 400 mL). The combined organic layers were dried over Na_2SO_4. Evaporation under reduced pressure afforded **SI-21** (6.54 g, 16.9 mmol, 94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09–7.07 (m, 3H), 3.59 (sept, J = 6.6, 2H), 2.62 (s, 2H), 2.09 (br s, 3H), 1.72–1.57 (br m, 14H), 1.18 (d, J = 6.0, 12H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 140.9, 124.1, 123.0, 55.6, 52.7, 50.0, 43.4, 37.0, 29.9, 28.0, 26.9, 24.4; HRMS-FAB (*m*/*z*) $[M + H]^+$ calcd for $C_{26}H_{43}N_2$, 383.3426; found, 383.3417.

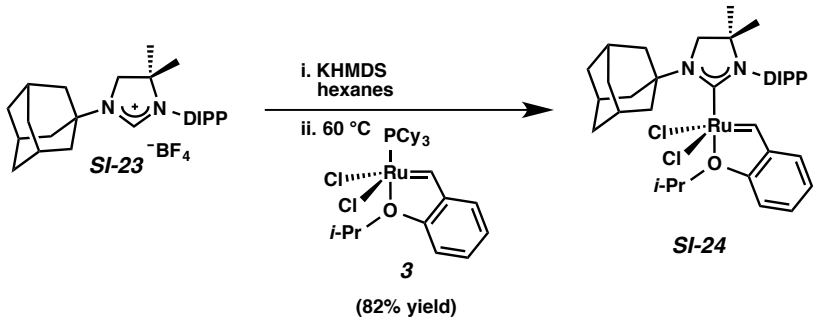


Formamidinium salt SI-22. To solution of diamine **SI-21** (300 mg, 0.776 mmol, 1.00 equiv) in Et_2O (5 mL) was added HCl (4.0 M in dioxane, 3.00 mL, 12.0 mmol, 15.5 equiv). The resulting white precipitate was isolated and washed with Et_2O, and then dried under reduced pressure to provide the HCl salt as white powder. The HCl salt of **SI-21** was transferred to a vial, to which was added MeCN (2 mL) and triethylorthoformate (2.00 mL, 12.0 mmol, 15.5 equiv). The vial was sealed with a PFTE cap and placed in a heating block maintained at 90 °C for 21 h. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. Et_2O (10 mL) was added to the concentrated solution and the resulting white precipitate

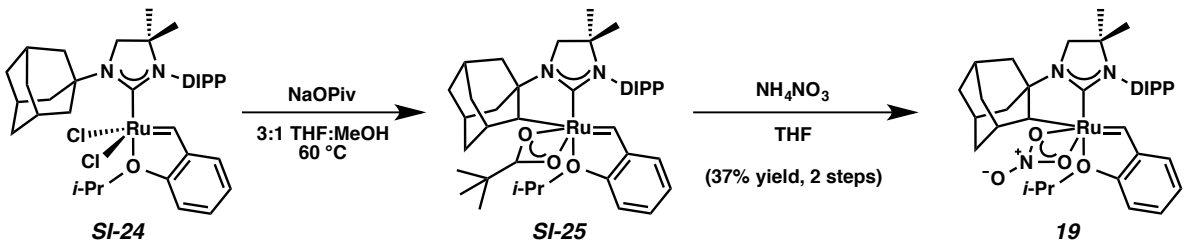
was isolated and washed with Et_2O to provide formamidinium salt **SI-22** (170 mg, 0.397 mmol, 66% yield, 2 steps) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.32 (t, *J* = 7.8, 1H), 7.16 (d, *J* = 7.8, 2H), 4.07 (s, 2H), 2.80 (sept, *J* = 6.6, 2H), 2.15 (br s, 3H), 2.06–2.05 (m, 6H), 1.69–1.59 (m, 6H), 1.36 (s, 6H), 1.22 (d, *J* = 6.9, 6H), 1.15 (d, *J* = 6.6, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 148.1, 130.7, 127.0, 124.8, 68.8, 58.8, 57.6, 41.0, 35.3, 29.4, 29.1, 26.5, 26.0, 22.8; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{27}H_{41}N_2$, 393.3279; found, 393.3277.



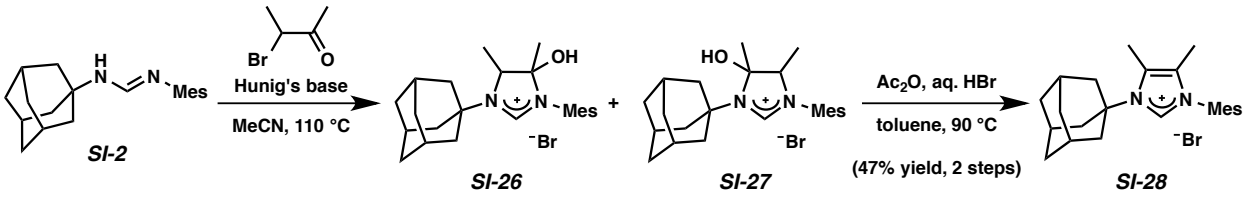
BF_4 Salt SI-23. To a solution of formamidinium salt **SI-22** (193 mg, 0.449 mmol, 1.00 equiv) in acetone (4 mL) and H_2O (4 mL) was added $NaBF_4$ (78.9 mg, 0.718 mmol, 1.60 equiv). The solution was stirred at 23 °C for 2 h, and then diluted with H_2O (20 mL) and CH_2Cl_2 (20 mL). The layers were separated, and then the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded **SI-23** (194 mg, 0.403 mmol, 90% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.43 (t, *J* = 8.0, 1H), 7.26 (d, *J* = 7.5, 2H), 4.13 (s, 2H), 2.92 (sept, *J* = 7.0, 2H), 2.25 (br s, 3H), 2.07 (app. s, 6H), 1.76–1.70 (m, 6H), 1.45 (s, 6H), 1.31 (d, *J* = 6.5, 6H), 1.17 (d, *J* = 7.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6, 148.5, 131.1, 127.1, 125.2, 69.5, 58.2, 57.6, 40.9, 35.5, 29.5, 29.3, 26.5, 26.1, 23.0; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{27}H_{41}N_2$, 393.3270; found, 393.3252.



Dichloride SI-24. In a glovebox, a Schlenk flask containing a solution of BF_4 salt **SI-23** (194 mg, 0.403 mmol, 2.36 equiv) in hexanes (10 mL) was treated with KHMDS (78.0 mg, 0.390 mmol, 2.28 equiv). The mixture was allowed to stir at 23 °C for 5 h, and was then treated with **3** (102 mg, 0.171 mmol, 1.00 equiv). After stirring for 21 h at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The precipitated solids were filtered and washed with hexanes, and then taken up in 1:1 Benzene:Et_2O and passed through a silica plug. Evaporation of the solvent under reduced pressure afforded **SI-24** (100 mg, 0.141 mmol, 82% yield) as a green powder. ^{1}H NMR (500 MHz, C_6D_6): δ 17.14 (s, 1H), 7.40 (t, *J* = 8.0, 1H), 7.30 (d, *J* = 7.5, 2H), 7.19–7.15 (m, 1H), 7.09 (dd, *J* = 7.5, 1.5, 1H), 6.70 (td, *J* = 7.5, 0.5, 1H), 6.44 (d, *J* = 8.5, 1H), 4.55 (sept, *J* = 6.0, 1H), 3.36 (sept, *J* = 6.5, 2H), 3.26 (s, 2H), 3.00 (br s, 6H), 2.32 (s, 3H), 1.93 (d, *J* = 12.0, 3H), 1.70 (d, *J* = 12.5, 3H), 1.60 (d, *J* = 6.0, 6H), 1.23 (d, *J* = 7.0, 6H), 1.08 (d, *J* = 6.5, 6H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6, 23/24 C): 210.4, 153.4, 150.7, 144.8, 137.6, 129.8, 129.2, 125.7, 123.7, 122.5, 113.6, 74.2, 64.7, 59.2, 57.3, 42.3, 36.4, 30.6, 28.6, 27.0, 26.0, 25.5, 22.6; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{37}H_{52}Cl_2N_2ORu$, 712.2500; found, 712.2488.



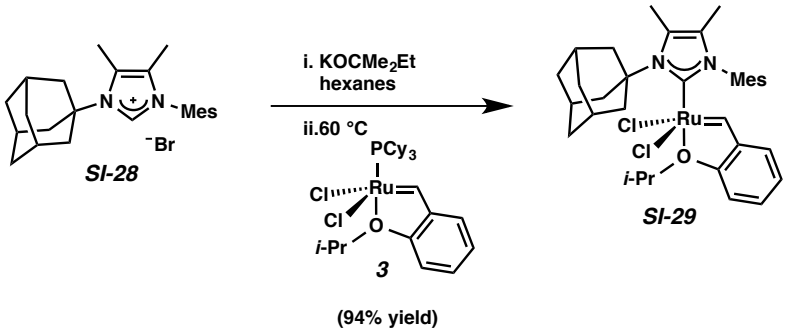
Nitrate 19. In a glovebox, a Schlenk flask containing a solution of **SI-24** (71.6 mg, 0.100 mmol, 1.00 equiv) in 3:1 THF:MeOH (4 mL) was treated with NaOPiv (124 mg, 1.00 mmol, 10.0 equiv). After stirring for 4 d at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The purple mixture was concentrated under reduced pressure, then taken up in THF (15 mL) and filtered through celite. The filtrate was treated with NH_4NO_3 (120 mg, 1.50 mmol, 15.0 equiv) and allowed to stir for 3.5 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated and triturated with Et_2O until the washes became colorless providing **19** as a purple solid (25.9 mg, 0.0368 mmol, 37 % yield, 2 steps). A crystal suitable for X-ray crystallography was prepared by recrystallization of **19** in a solution of Et_2O. ^{1}H NMR (400 MHz, C_6D_6): δ 15.10 (s, 1H), 7.37 (d, *J* = 7.6, 1H), 7.25 (t, *J* = 7.6, 1H), 7.19–7.16 (m, 2H), 7.10 (d, *J* = 7.2, 1H), 6.83 (t, *J* = 7.6, 1H), 6.50 (d, *J* = 8.4, 1H), 4.63 (sept, *J* = 6.4, 1H), 4.17 (s, 1H), 3.88 (sept, *J* = 6.8, 1H), 3.32 (d, *J* = 10.4, 1H), 2.95 (sept, *J* = 6.8, 1H), 2.79 (d, *J* = 10.4, 1H), 2.37 (s, 1H), 2.11 (s, 1H), 1.99–1.95 (m, 2H), 1.85 (d, *J* = 9.6, 1H), 1.77 (d, *J* = 12.0, 1H), 1.72 (d, *J* = 6.8, 3H), 1.64 (s, 1H), 1.57–1.49 (s, 2H), 1.43 (d, *J* = 6.4, 3H), 1.40 (s, 3H), 1.39–1.35 (m, 1H), 1.26 (d, *J* = 6.8, 3H), 1.20 (d, *J* = 6.4, 3H), 1.16–1.10 (m, 2H), 1.07 (d, *J* = 6.4, 3H), 0.99 (d, *J* = 6.0, 3H), 0.97 (s, 3H), 0.57 (br d, *J* = 12.0, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 267.0, 211.3, 154.8, 149.27, 149.26, 143.6, 133.5, 129.2, 126.7, 125.4, 125.0, 123.5, 123.4, 113 .5, 74.9, 66.8, 66.7, 62.8, 55.1, 42.9, 40.3, 38.02, 37.95, 37.7, 33.4, 31.4, 30.9, 29.9, 29.5, 28.7, 2 6.7, 26.2, 24.8, 24.7, 23.2, 21.1, 20.4; HRMS-FAB (*m/z*) $[(M + H)–H_2]^+$ calcd for $C_{37}H_{50}N_3O_4Ru$, 702.2855; found, 702.2845.



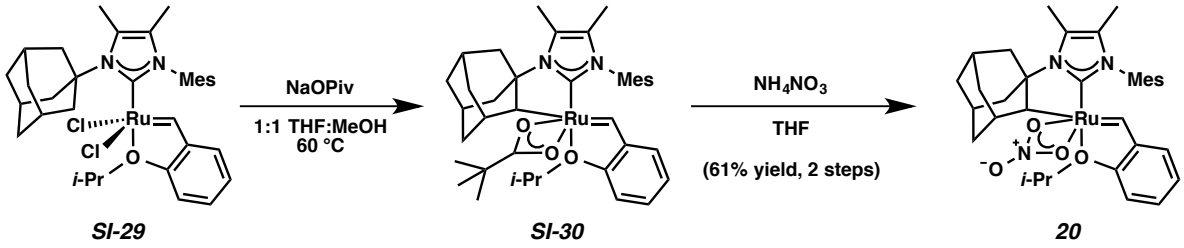
1,3-Dimethyl Imidazolium Salt SI-28. Imidazolium salt **SI-28** was prepared following a known procedure,[5] with minor modifications. To a pressure tube was added adamantyl mesityl

formamidine **SI-2**[6] (1.70 g, 5.75 mmol, 1.00 equiv), MeCN (11.5 mL), Hunig's base (1.20 mL, 6.90 mmol, 1.20 equiv), and then 3-bromo-2-butanone (0.60 mL, 5.60 mmol, 0.97 equiv). The vial was sealed and heated to 110 °C. The solution was stirred for 1 d and then cooled to room temperature. Additional 3-bromo-2-butanone (1.00 mL, 9.34 mmol, 1.60 equiv) was added, the mixture was stirred at 110 °C for 1 day and then cooled to room temperature. Evaporation of the solvent under reduced pressure afforded crude regioisomers **SI-26** and **SI-27**, which were used in the subsequent step without further purification.

Crude regioisomers **SI-26** and **SI-27**, still contained within a pressure tube, were dissolved in toluene (14.3 mL) and aq. HBr (38% w/w, 0.760 mL, 8.62 mmol, 1.50 equiv) followed by Ac_2O (1.63 mL, 17.2 mmol, 3.00 equiv) were added. The vial was sealed and heated to 90 °C. The solution was stirred for 1 d, cooled to room temperature, and then diluted with H_2O (100 mL) and with CH_2Cl_2 (100 mL). The layers were separated, and then the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over $MgSO_4$, then concentrated to dryness *in vacuo*. The resulting oil was taken up in CH_2Cl_2 (20 mL), and Et_2O was added until white solids crashed out of solution. The mixture was filtered through a fritted funnel, and the product was washed with Et_2O and then dried under reduced pressure to give **SI-28** (1.16 g, 2.70 mmol, 47% yield, 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.01 (s, 2H), 2.61 (d, *J* = 0.5, 3H), 2.47 (d, *J* = 2.5, 6H), 2.35 (br s, 3H), 2.33 (s, 3H), 2.04 (s, 6H), 1.94 (d, *J* = 0.5, 3H), 1.84 (d, *J* = 11.5, 3H), 1.77 (d, *J* = 12.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.1, 135.2, 135.0, 129.9, 129.2, 129.1, 126.5, 63.8, 41.7, 35.4, 29.8, 21.3, 18.1, 13.1; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{24}H_{33}N_2$, 349.2644; found, 349.2627.

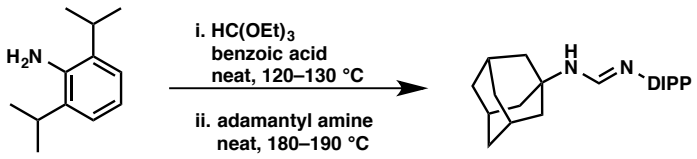


Ruthenium Dichloride SI-29. In a glove box, a Schlenk flask containing a solution of 1,3-dimethyl imidazolium salt **SI-28** (173 mg, 0.403 mmol, 1.20 equiv) in hexanes (5 mL) was treated with $KOCMe_2Et$ (50.9 mg, 0.403 mmol, 1.20 equiv). The mixture was allowed to stir at 23 °C for 3.5 h, and was then treated with **3** (202 mg, 0.336 mmol, 1.00 equiv). After stirring for 17 h at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The precipitated solids were filtered and washed with hexanes to provide **SI-29** as a green powder (210 mg, 0.314 mmol, 94% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 17.36 (s, 1H), 7.27–7.23 (m, 2H), 6.83–6.80 (m, 3H), 6.50 (dd, J = 8.5, 0.5, 1H), 4.58 (sept, J = 7.0, 1H), 2.49–2.02 (m, 23H), 1.71–1.58 (m, 10H), 1.48 (d, J = 0.5, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ 308.3, 217.8, 169.7, 152.9, 147.2, 139.1, 138.5, 137.8, 129.6, 129.5, 129.4, 128.6, 126.6, 122.9, 113.6, 74.3, 61.0, 41.6, 36.4, 22.6, 21.2, 18.7, 14.9, 9.1; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{34}H_{44}N_2ORuCl_2$, 668.1875; found, 668.1867.



Nitrate 20. In a glovebox, a Schlenk flask containing a solution of **SI-29** (88.7 mg, 0.133 mmol, 1.00 equiv) in 1:1 THF:MeOH (4 mL) was treated with NaOPiv (165 mg, 1.33 mmol, 10.0

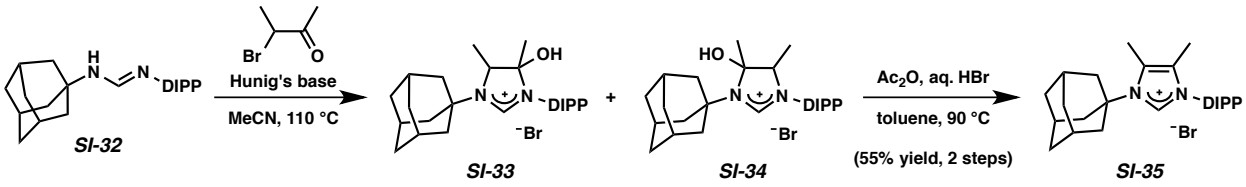
equiv). After stirring for 1 d at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The purple mixture was concentrated under reduced pressure, then taken up in THF (15 mL) and filtered through celite. The filtrate was treated with NH_4NO_3 (160 mg, 2.00 mmol, 15.0 equiv) and allowed to stir for 3 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated and triturated with pentane until the washes became colorless. The resulting solid was dissolved in minimal Et_2O and benzene, and pentanes were added until the solution became opaque. The mixture was placed in the glove box freezer overnight, and white solids were removed by filtration. The filtrate was concentrated under reduced pressure to give **20** as a periwinkle solid (53.5 mg, 0.0812 mmol, 61% yield, 2 steps). ^{1}H NMR (400 MHz, C_6D_6): δ 15.60 (s, 1H), 7.43 (d, *J* = 7.6, 1H), 7.22 (t, *J* = 7.6, 1H), 6.99 (s, 1H), 6.84 (t, *J* = 7.6, 1H), 6.68 (s, 1H), 6.52 (d, *J* = 8.4, 1H), 4.58 (sept, *J* = 6.0, 1H), 4.44 (s, 1H), 2.59–2.57 (m, 1H), 2.29–1.99 (m, 18H), 1.81–1.62 (m, 4H), 1.51 (s, 3H), 1.45 (d, *J* = 6.5, 3H), 1.07 (br d, *J* = 13.0, 1H), 0.99 (d, *J* = 6.0, 3H), 0.66 (br d, *J* = 12.8, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 264.4, 180.5, 154.5, 143.6, 137.7, 136.6, 134.5, 133.9, 129.5, 128.9, 126.1, 125.2, 123.0, 122.9, 122.7, 112.6, 73.8, 67.5, 66.2, 43.2, 39.8, 39.6, 37.8, 37.6, 32.3, 30.7, 29.7, 20.9, 20.7, 19.9, 18.0 , 17.1, 10.3, 8.2; HRMS-FAB (*m/z*) $[(M + H)–H_2]^+$ calcd for $C_{34}H_{42}N_3O_4Ru$, 658.2219; found, 658.2245.



SI-31 **(47% yield)** ***SI-32***

Adamantyl Diisopropyl Formamidine SI-32. To a round bottom flask was added 2,6-diisopropylaniline (**SI-31**, 11.3 mL, 60.0 mmol, 1.00 equiv), triethyl orthoformate (10.0 mL, 60.0 mmol, 1.00 equiv), and benzoic acid (312 mg, 2.55 mmol, 4.25 mol%). The flask was affixed with a short path distillation apparatus, and the mixture was heated to ~120–130 °C. EtOH was distilled off over 2 h, after which the mixture was cooled to room temperature. Adamantyl amine

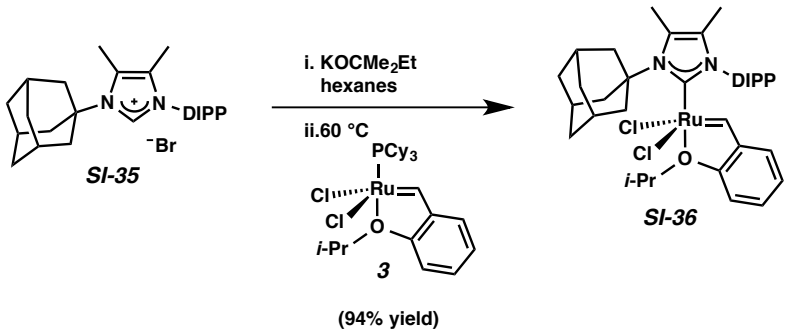
(9.03 g, 60.0 mmol, 1.00 equiv) was added, the distillation apparatus was reassembled, and the resulting mixture was heated to ~180–190 °C. The solution was stirred for 22 h and then cooled to room temperature. The resulting solid mixture was filtered through a fritted funnel, and the product was washed with hexanes and then dried under reduced pressure to give **SI-32** (3.63 g). The filtrate was collected and partially concentrated under reduced pressure, and the resulting solution was placed in the freezer overnight. Additional solids that precipitated from solution were isolated and washed with hexanes, then dried under reduced pressure to give **SI-32** as a white solid (5.91 g, 9.53 g total collected, 28.2 mmol, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of isomers): δ 7.49–7.46 (m, 0.5H), 7.34 (br s, 0.5H), 7.13–7.01 (m, 3H), 3.15 (sept, J = 7.0, 1H), 3.05 (sept, J = 7.0, 1H), 2.10 (br s, 3H), 1.84 (br s, 3H), 1.71–1.58 (m, 10H), 1.19–1.16 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of isomers): δ 149.8 (N=CH–N), 144.5, 143.5, 140.8 (N=CH–N), 139.5, 123.4, 123.2, 122.9, 50.7, 44.3, 36.3, 36.1, 29.6, 29.5, 27.9, 24.0, 23.9, 23.8; HRMS-FAB (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{35}N_2$, 339.2800; found, 339.2809.



1,3-Dimethyl Imidazolium Salt SI-35. Imidazolium salt **SI-35** was prepared following a known procedure,[5] with minor modifications. To a pressure tube was added adamantyl diisopropyl formamidine **SI-32** (1.80 g, 5.30 mmol, 1.00 equiv), MeCN (10.6 mL), Hunig's base (1.12 mL, 6.36 mmol, 1.20 equiv), and then 3-bromo-2-butanone (1.14 mL, 10.6 mmol, 2.00 equiv). The vial was sealed and heated to 110 °C. The solution was stirred for 1 d and then cooled to room temperature. Evaporation of the solvent under reduced pressure afforded crude regioisomers **SI-33** and **SI-34**, which were used in the subsequent step without further purification.

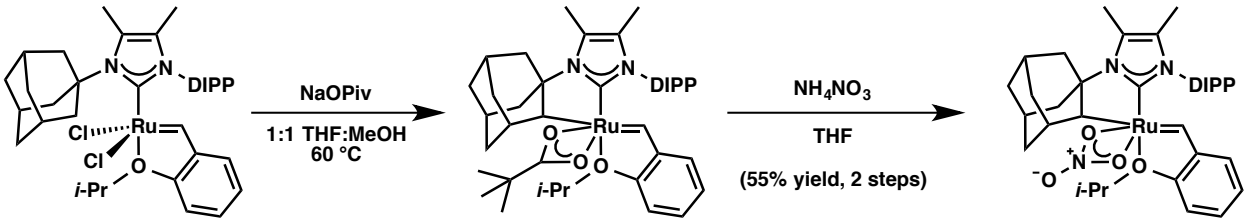
Crude regioisomers **SI-33** and **SI-34**, still contained within a pressure tube, were dissolved in toluene (13 mL) and aq. HBr (38% w/w, 0.700 mL, 7.95 mmol, 1.50 equiv) followed by Ac_2O (1.50 mL, 15.9 mmol, 3.00 equiv) were added. The vial was sealed and heated to 90 °C. The

solution was stirred for 1 d, cooled to room temperature, and then diluted with H_2O (100 mL) and with CH_2Cl_2 (100 mL). The layers were separated, and then the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over $MgSO_4$, then concentrated to dryness *in vacuo*. The resulting oil was taken up in CH_2Cl_2 (20 mL), and Et_2O was added until white solids crashed out of solution. The mixture was filtered through a fritted funnel, and the product was washed with Et_2O and then dried under reduced pressure to give **SI-35** (1.38 g, 2.93 mmol, 55% yield, 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.54 (t, *J* = 8.0, 1H), 7.33 (d, *J* = 8.0, 2H), 2.68 (d, *J* = 1.0, 3H), 2.48 (d, *J* = 3.0, 6H), 2.38 (br s, 3H), 2.20 (sept, *J* = 7.0, 2H), 1.98 (d, *J* = 0.5, 3H), 1.87 (d, *J* = 13.0, 3H), 1.79 (d, *J* = 12.5, 3H), 1.29 (d, *J* = 7.0, 6H), 1.18 (d, *J* = 7.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.7, 135.3, 132.0, 130.2, 128.6, 127.0, 125.0, 64.2, 42.1, 35.4, 29.8, 28.9, 25.3, 23.6, 13.4, 8.9; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{27}H_{39}N_2$, 391.3113; found, 391.3118.



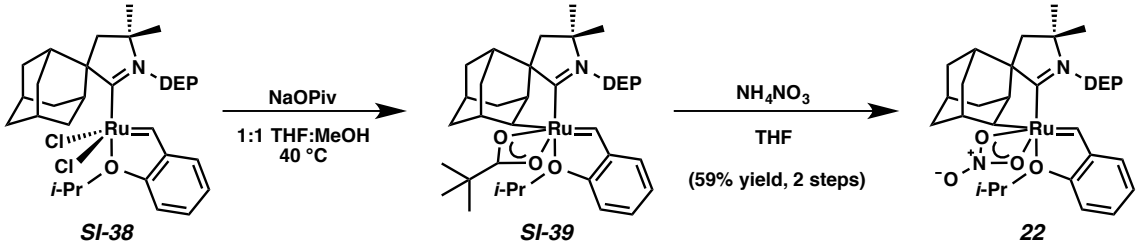
Ruthenium Dichloride SI-36. In a glove box, a Schlenk flask containing a solution of 1,3-dimethyl imidazolium salt **SI-35** (190 mg, 0.403 mmol, 1.20 equiv) in hexanes (5 mL) was treated with $KOCMe_2Et$ (50.9 mg, 0.403 mmol, 1.20 equiv). The mixture was allowed to stir at 23 °C for 5 h, and was then treated with **3** (202 mg, 0.336 mmol, 1.00 equiv). After stirring for 25.5 h at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The precipitated solids were filtered and washed with hexanes to provide **SI-36** as a green powder (244 mg, 0.314 mmol, 94% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 17.50 (s, 1H), 7.46 (t, *J* = 7.6, 1H), 7.30 (d, *J* = 7.6, 2H), 7.25–7.20 (m, 2H), 6.76 (t, *J* = 7.2, 1H), 6.48

(d, J = 7.2, 1H), 4.56 (sept, J = 5.2, 1H), 2.98 (sept, J = 6.8, 2H), 2.93–1.33 (br m, 27H), 1.12 (d, J = 6.8, 6H), 0.95 (d, J = 7.2, 6H); ^{13}C NMR (100 MHz, C_6D_6, 24/25 C): δ 170.6, 153.2, 148.6, 146.2, 137.9, 131.2, 130.3, 129.4, 126.4, 125.2, 123.1, 122.7, 113.7, 74.2, 61.3, 41.7, 36.3, 30.8, 28.2, 25.0, 24.6, 22.7, 15.1, 10.5; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{37}H_{50}N_2ORuCl_2$, 710.2344; found, 710.2374.



Nitrate 21. In a glovebox, just prior to performing C–H activation, dichloride **SI-36** was taken up in CH_2Cl_2 and filtered over SiO_2, then concentrated under reduced pressure.[7] A Schlenk flask containing a solution of **SI-36** (36.1 mg, 0.0509 mmol, 1.00 equiv) in 1:1 THF:MeOH (4 mL) was treated with NaOPiv (63.2 mg, 0.509 mmol, 10.0 equiv). After stirring for 2 d at 60 °C outside the glove box, the flask was cooled to room temperature and transferred back to the glove box. The purple mixture was concentrated under reduced pressure, then taken up in THF (10 mL) and filtered through celite. The filtrate was treated with NH_4NO_3 (70.8 mg, 0.885 mmol, 15.0 equiv) and allowed to stir for 3 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated and triturated with pentane, followed by Et_2O until the washes became colorless providing **21** as a periwinkle solid (22.9 mg, 0.0327 mmol, 55 % yield, 2 steps). A crystal suitable for X-ray crystallography was prepared by recrystallization via slow diffusion of pentane into a solution of **21** in THF. ^{1}H NMR (400 MHz, C_6D_6): δ 15.48 (s, 1H), 7.50 (d, J = 7.6, 1H), 7.30–7.20 (m, 3H), 7.05 (d, J = 7.6, 1H), 6.87 (t, J = 7.6, 1H), 6.51 (d, J = 8.4, 1H), 4.58 (sept, J = 6.4, 1H), 4.44 (s, 1H), 3.44 (sept, J = 6.8, 1H), 2.60–2.54 (m, 2H), 2.37 (s, 1H), 2.06–1.97 (m, 6H), 1.77–1.65 (m, 9H), 1.47 (d, J = 6.0, 6H), 1.15 (d, J = 6.8, 3H), 1.11–1.08 (m, 4H), 1.01 (d, J = 6.4, 6H), 0.64 (br d, J = 13.2, 1H); ^{13}C NMR (100 MHz, C_6D_6):

δ 266.4, 181.2, 155.1, 146.9, 146.6, 143.8, 133.6, 130.0, 127.2, 126.6, 124.8, 124.4, 123.5, 123.3, 123.2, 113.3, 74.5, 67.9, 66.2, 44.0, 40.0, 38.9, 38.2, 38.1, 32.9, 31.1, 30.1, 29.0, 28.6, 25.9, 25.3, 24.2, 23.7, 21.2, 20.4, 10.6, 9.9; HRMS-FAB (*m*/*z*) $[(M + H)–H_2]^+$ calcd for $C_{37}H_{48}N_3O_4Ru$, 700.2689; found, 700.2690.

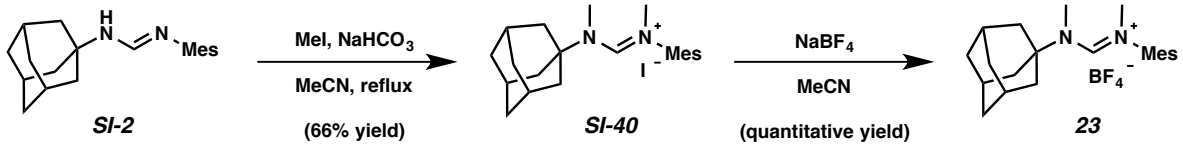


SI-38 *SI-39* *22*

Nitrate 22. In a glovebox, a vial containing a solution of **SI-38**[8] (50 mg, 0.075 mmol, 1.0 equiv) in 1:1 THF:MeOH (2 mL) was treated with NaOPiv (100 mg, 0.80 mmol, 10.7 equiv). After stirring for 3 h at 40 °C, the reaction mixture was cooled to room temperature. The mixture was concentrated under reduced pressure, then taken up in pentane and filtered through celite. The filtrate was concentrated, dissolved in THF (4 mL) and then treated with NH_4NO_3 (80 mg, 0.80 mmol, 10.7 equiv) and allowed to stir for 1.5 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was then concentrated to give **22** (30 mg, 0.044 mmol, 59% yield, 2 steps) as a brown solid. A crystal suitable for X-ray crystallography was prepared by recrystallization via slow diffusion of pentane into a solution of **22** in Et_2O. ^{1}H NMR (500 MHz, C_6D_6): δ 14.24 (s, 1H), 7.27–7.22 (m, 3H), 7.16–7.13 (m, 1H), 6.95 (dd, *J* = 7.7, 1.2, 1H), 6.78 (td, *J* = 7.4, 0.8, 1H), 6.46 (d, *J* = 8.4, 1H), 4.58 (sept d, *J* = 6.0, 0.5, 1H), 3.36 (td, *J* = 3.6, 1.5, 1H), 3.10 (br d sept, *J* = 13.0, 2.0, 1H), 2.83 (ddq, *J* = 19.7, 15.1, 7.5, 2H), 2.69 (dq, *J* = 14.8, 7.5, 1H), 2.56 (dq, *J* = 15.0, 7.4, 1H), 2.40–2.38 (m, 1H), 2.20 (d, *J* = 12.5, 1H), 2.14 (br s, 2H), 2.09 (dq, *J* = 12.2, 3.1, 1H), 2.04–2.00 (m, 1H), 1.99–1.95 (m, 2H), 1.91–1.78 (m, 4H), 1.65 (d, *J* = 12.8, 1H), 1.34 (d, *J* = 6.3, 3H), 1.27 (t, *J* = 7.5, 3H), 1.12 (s, 3H), 1.08 (d, *J* = 6.3, 3H), 1.07 (s, 3H), 0.98 (t, *J* = 7.5, 3H); ^{13}C NMR (125 MHz, C_6D_6): 267.4, 154.7, 143.6, 142.9, 141.2, 137.1, 128.6, 126.82, 126.76, 123.2, 123.1, 113.6, 76.5, 75.5, 72.1, 58.5, 51.1, 48.0, 40.4, 37.9,

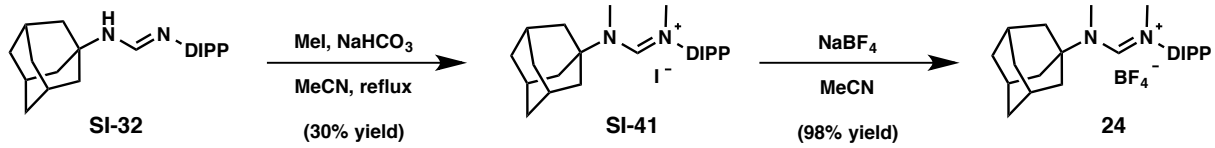
36.2, 35.8, 34.2, 31.6, 28.2, 28.0, 26.2, 23.6, 21.6, 20.5, 15.6, 14.1; HRMS-FAB (*m/z*) [(M + H)–H_2]$^+$ calcd for $C_{35}H_{45}N_2O_4Ru$, 659.2423; found, 659.2436.

B. Synthesis of Formamidinium Salts in Figure 3



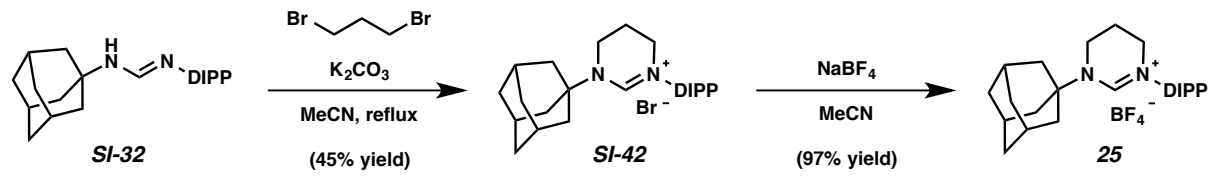
Formamidinium salt 23. To a microwave vial containing a solution of formamidine **SI-2**[6] (430 mg, 1.45 mmol, 1.00 equiv) in MeCN (3.0 mL) was added $NaHCO_3$ (610 mg, 7.25 mmol, 5.00 equiv) and methyl iodide (0.270 mL, 4.35 mmol, 3.00 equiv). The reaction vessel was sealed and placed in a microwave reactor, and allowed to stir at 180 °C for 40 min. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting solids were taken up in CH_2Cl_2 and passed through a fritted filter to remove $NaHCO_3$. The filtrate was concentrated under reduced pressure, and taken up CH_2Cl_2 (5 mL) followed by Et_2O (20 mL) and the resulting solution was placed in the freezer overnight. Slightly yellow solids that precipitated from solution were isolated and washed with Et_2O, then dried under reduced pressure to give **SI-40** (430 mg, 0.950 mmol, 66% yield)**.**

SI-40 (310 mg, 0.685 mmol, 1.00 equiv) was taken up in MeCN (4.0 mL) and treated with $NaBF_4$ (752 mg, 6.85 mmol, 10.0 equiv), and was stirred at 23 °C for 2.5 h. The solution was filtered over celite and washed through with CH_2Cl_2. Evaporation of the solvent under reduced pressure afforded **23** (280 mg, 0.679 mmol, quantitative yield) as a slightly yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 1H), 6.95 (s, 2H), 3.80 (s, 3H), 2.40 (s, 3H), 2.32–2.20 (m, 12H), 2.16 (d, *J* = 2.9, 6H), 1.75 (d, *J* = 12.6, 3H), 1.71 (d, *J* = 12.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.1, 140.1, 136.5, 134.3, 130.0, 64.8, 47.3, 40.5, 35.5, 30.1, 29.8, 21.1, 18.4; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{22}H_{33}N_2$, 325.2644; found, 325.2632.



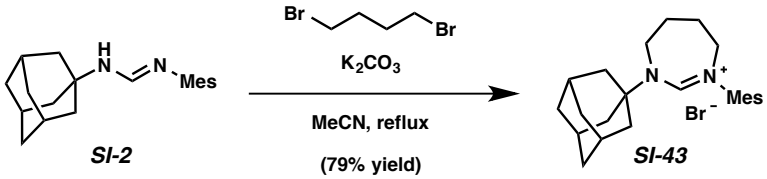
Formamidinium salt 24. To Schlenk flask containing a solution of formamidine **SI-32**[9] (480 mg, 1.40 mmol, 1.00 equiv) in MeCN (3.0 mL) was added $NaHCO_3$ (590 mg, 7.00 mmol, 5.00 equiv) and methyl iodide (0.265 mL, 4.30 mmol, 3.00 equiv). The reaction vessel was sealed and placed in a heating bath maintained at 85 °C for 13 h. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting solids were taken up in CH_2Cl_2 and passed through a fritted filter to remove $NaHCO_3$. The filtrate was concentrated under reduced pressure, and taken up CH_2Cl_2 (5 mL) followed by Et_2O (20 mL) and the resulting solution was placed in the freezer overnight. Slightly yellow solids that precipitated from solution were isolated and washed with Et_2O, then dried under reduced pressure to give **SI-41** (205 mg, 0.415 mmol, 30% yield).

SI-41 (201 mg, 0.407 mmol, 1.00 equiv) was taken up in MeCN (2.5 mL) and treated with $NaBF_4$ (446 mg, 4.07 mmol, 10.0 equiv), and was stirred at 23 °C for 2.5 h. The solution was filtered over celite and washed through with CH_2Cl_2. Evaporation of the solvent under reduced pressure afforded **24** (180 mg, 0.396 mmol, 98% yield) as a slightly yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.44 (t, J = 7.8, 1H), 7.24 (d, J = 7.8, 2H), 3.88 (s, 3H), 3.07 (sept, J = 6.8, 2H), 2.42 (s, 3H), 2.30 (br s, 3H), 2.16 (d, J = 2.8, 6H), 1.75 (d, J = 12.0, 3H), 1.70 (d, J = 12.8, 3H), 1.28 (d, J = 6.8, 6H), 1.24 (d, J = 6.8, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 145.0, 136.1, 130.9, 125.4, 65.2, 49.7, 40.5, 35.4, 30.4, 29.8, 28.7, 25.4, 23.6; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{25}H_{39}N_2$, 367.3113; found, 367.3112.



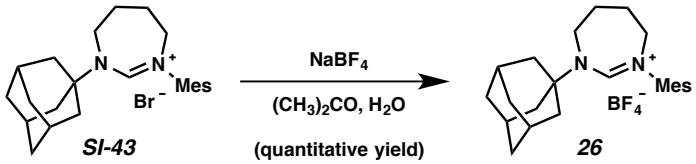
Formamidinium salt 25. To solution of formamidine **SI-32**[9] (750 mg, 2.22 mmol, 1.00 equiv) in MeCN (80 mL) was added K_2CO_3 (156 mg, 1.13 mmol, 0.51 equiv) and 1,3-dibromopropane (0.249 mL, 2.44 mmol, 1.10 equiv). The reaction vessel was placed in a heating bath maintained at 85 °C for 16 h. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting solids were taken up in CH_2Cl_2 and passed through a fritted filter to remove K_2CO_3. The filtrate was concentrated under reduced pressure, and taken up CH_2Cl_2 (20 mL) followed by Et_2O (100 mL) and the resulting solution was placed in the freezer overnight. White solids that precipitated from solution were isolated and washed with Et_2O, then dried under reduced pressure to give **SI-42** (483 mg, 1.05 mmol, 45% yield).

To a solution of formamidinium salt **SI-42** (93.0 mg, 0.203 mmol, 1.00 equiv) in MeCN (1.0 mL) was added $NaBF_4$ (222 mg, 2.0 mmol, 10 equiv). The solution was stirred at 23 °C for 2 h, and then diluted with H_2O (10 mL) and CH_2Cl_2 (10 mL). The layers were separated, and then the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine (10 mL), then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded **25** (92.0 mg, 0.197 mmol, 97% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.44 (t, *J* = 7.8, 1H), 7.27 (d, *J* = 7.7, 2H), 4.21 (t, *J* = 5.7, 2H), 3.87 (t, *J* = 5.7, 2H), 2.95 (sept, *J* = 6.8, 2H), 2.47 (pent, *J* = 5.7, 2H), 2.28 (br s, 3H), 2.00 (d, *J* = 2.8, 6H), 1.75 (br d, *J* = 12.5, 3H), 1.69 (br d, *J* = 12.0, 3H), 1.31 (d, *J* = 6.8, 6H), 1.23 (d, *J* = 6.8, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 146.1, 137.1, 131.1, 125.3, 62.2, 48.9, 40.8, 39.8, 35.5, 29.5, 28.8, 25.3, 24.2, 20.0; HRM S-FAB (*m/z*) $[M]^+$ calcd for $C_{26}H_{39}N_2$, 379.3113; found, 379.3102.



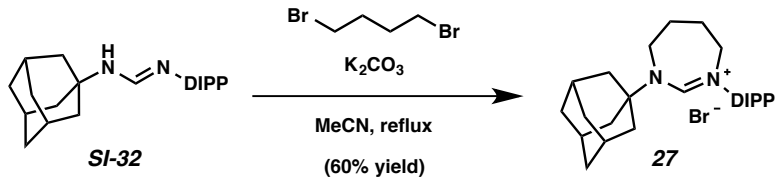
Formamidinium salt SI-43. Formamidinium salt **SI-43**[6] was prepared following a known procedure, with minor modifications.[10] To solution of formamidine **SI-2** (1.00 g, 3.71 mmol,

1.00 equiv) in MeCN (134 mL) was added K_2CO_3 (262 mg, 1.89 mmol, 0.51 equiv) and 1,4-dibromobutane (0.486 mL, 4.08 mmol, 1.10 equiv). The reaction vessel was placed in a heating bath maintained at 85 °C for 23 h. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting solids were taken up in CH_2Cl_2 and passed through a fritted filter to remove K_2CO_3. The filtrate was concentrated under reduced pressure, and taken up CH_2Cl_2 (20 mL) followed by Et_2O (100 mL) and the resulting solution was placed in the freezer overnight. White solids that precipitated from solution were isolated and washed with Et_2O, then dried under reduced pressure to give **SI-43** (1.04 g, 2.95 mmol, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (s, 1H), 6.95 (d, *J* = 1.0, 2H), 4.41–4.39 (m, 2H), 4.29–4.27 (m, 2H), 2.38–2.36 (m, 8H), 2.31–2.25 (m, 8H), 2.32–2.25 (m, 6H), 1.73 (d, *J* = 12.5, 3H), 1.68 (d, *J* = 13.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 140.2, 140.0, 134.3, 130.3, 63.3, 53.5, 44.7, 40.9, 35.4, 29.6, 25.5, 25.0, 21.1, 18.7; HRMS-FAB (*m*/*z*) $[M]^+$ calcd for $C_{24}H_{35}N_2$, 351.2800; found, 351.2815.



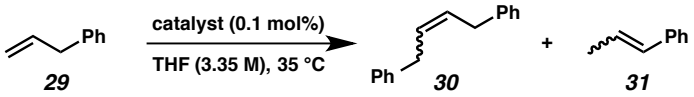
BF_4 Salt 26. To a solution of formamidinium salt **SI-43** (676 mg, 1.57 mmol, 1.00 equiv) in acetone (6.7 mL) and H_2O (3.4 mL) was added $NaBF_4$ (275 mg, 2.51 mmol, 1.60 equiv). The solution was stirred at 23 °C for 1 h, and then diluted with H_2O (40 mL) and CH_2Cl_2 (40 mL). The layers were separated, and then the aqueous layer was extracted with CH_2Cl_2 (2 × 40 mL). The combined organic layers were washed with brine (40 mL), then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded **26** (719 mg, quantitative yield) as a white solid. ^{1}H NMR (500 MHz, C_6D_6): δ 7.04 (s, 1H), 6.71 (s, 2H), 4.04 (t, *J* = 5.5, 2H), 3.78 (t, *J* = 5.0, 2H), 2.26 (s, 6H), 2.06–2.04 (m, 7H), 1.90 (br s, 3H), 1.57 (s, 6H), 1.51 (d, *J* = 12.5, 3H), 1.41 (d, *J* = 12.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 141.0, 139.3, 135.1, 130.2,

62.8, 53.0, 44.1, 39.7, 35.4, 29.8, 25.4, 24.9, 20.9, 18.2; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{24}H_{35}N_2$, 351.2800; found, 351.2791.

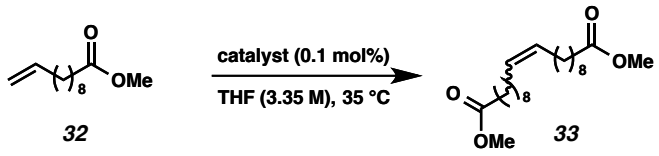


Formamidinium salt 27. Formamidinium salt **27**[9] was prepared following a known procedure, with minor modifications.[10] To solution of formamidine **SI-22** (500 mg, 1.48 mmol, 1.00 equiv) in MeCN (54 mL) was added K_2CO_3 (103 mg, 0.752 mmol, 0.51 equiv) and 1,4-dibromobutane (0.194 mL, 1.63 mmol, 1.10 equiv). The reaction vessel was placed in a heating bath maintained at 85 °C for 16.5 h. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting solids were taken up in CH_2Cl_2 and passed through a fritted filter to remove K_2CO_3. The filtrate was concentrated under reduced pressure, and taken up CH_2Cl_2 (20 mL) followed by Et_2O (100 mL) and the resulting solution was placed in the freezer overnight. White solids that precipitated from solution were isolated and washed with Et_2O, then dried under reduced pressure to give **27** (417 mg, 0.880 mmol, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, *J* = 7.8, 1H), 7.30 (s, 1H), 7.21 (d, *J* = 7.8, 2H), 4.40 (t, *J* = 5.8, 2H), 4.18 (t, *J* = 5.8, 2H), 3.03 (sept, *J* = 6.8, 2H), 2.40–2.35 (m, 2H), 2.34–2.29 (m, 2H), 2.22 (br s, 3H), 1.92 (d, *J* = 2.8, 6H), 1.68 (d, *J* = 12.7, 3H), 1.63 (d, *J* = 12.4, 3H), 1.29 (d, *J* = 6.8, 6H), 1.19 (d, *J* = 6.8, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 145.0, 139.5, 130.7, 125.3, 63.2, 54.9, 44.8, 40.7, 35.2, 29.4, 28.8, 25.3, 25.1, 24.5, 23.9; HRMS-FAB (*m/z*) $[M]^+$ calcd for $C_{27}H_{41}N_2$, 393.3270; found, 393.3267.

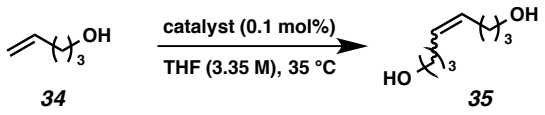
C. General Procedures for Homodimerization Assays



In a glovebox, a 4 mL vial was charged with Ru catalyst and THF to prepare a 0.009 M stock solution. A portion of the catalyst stock solution (111 μL, *ca*. 1.0 μmol, 0.1 mol%) was added to a 4 mL vial containing allyl benzene (**29**) (132 μL, 1.0 mmol), THF (92 μL), and a stir bar. The vial was then placed in a heating block maintained at 35 °C, and the reaction was stirred open to the glovebox atmosphere. Aliquots were removed from the glovebox at 1-, 3-, 7-, and 12-hour time points, were quenched with oxygen, and then diluted with $CDCl_3$. Conversion, extent of olefin isomerization, and *Z*-selectivity were calculated by analysis of the ^{1}H NMR spectra of the unpurified aliquot. Spectra were consistent with data in previous literature reports.[11]



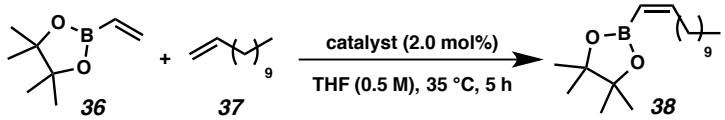
In a glovebox, a 4 mL vial was charged with Ru catalyst and THF to prepare a 0.009 M stock solution. A portion of the catalyst stock solution (111 μL, *ca*. 1.0 μmol, 0.1 mol%) was added to a 4 mL vial containing 10-methyl undecenoate (**32**) (225 μL, 1.00 mmol) and a stir bar. The vial was then placed in a heating block maintained at 35 °C, and the reaction was stirred open to the glovebox atmosphere. Aliquots were removed from the glovebox at 1-, 3-, 7-, and 12-hour time points, were quenched with oxygen, and then diluted with $CDCl_3$. Conversion and *Z*-selectivity were calculated by analysis of the ^{1}H NMR spectra of the unpurified aliquot. Spectra were consistent with data in previous literature reports.[11]



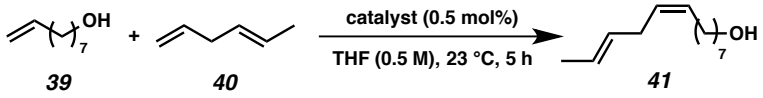
34 ***35***

In a glovebox, a 4 mL vial was charged with Ru catalyst and THF to prepare a 0.009 M stock solution. A portion of the catalyst stock solution (111 μL, *ca*. 1.0 μmol, 0.1 mol%) was added to a 4 mL vial containing 4-pentenol (**34**) (103 μL, 1.0 mmol), THF (121 μL), and a stir bar. The vial was then placed in a heating block maintained at 35 °C, and the reaction was stirred open to the glovebox atmosphere. Aliquots were removed from the glovebox at 1-, 3-, 7-, and 12-hour time points, were quenched with oxygen, and then diluted with $CDCl_3$. Conversion and *Z*-selectivity were calculated by analysis of the ^{1}H NMR spectra of the unpurified aliquot. Spectra were consistent with data in previous literature reports.[11]

D. General Procedures for Cross Metathesis Studies

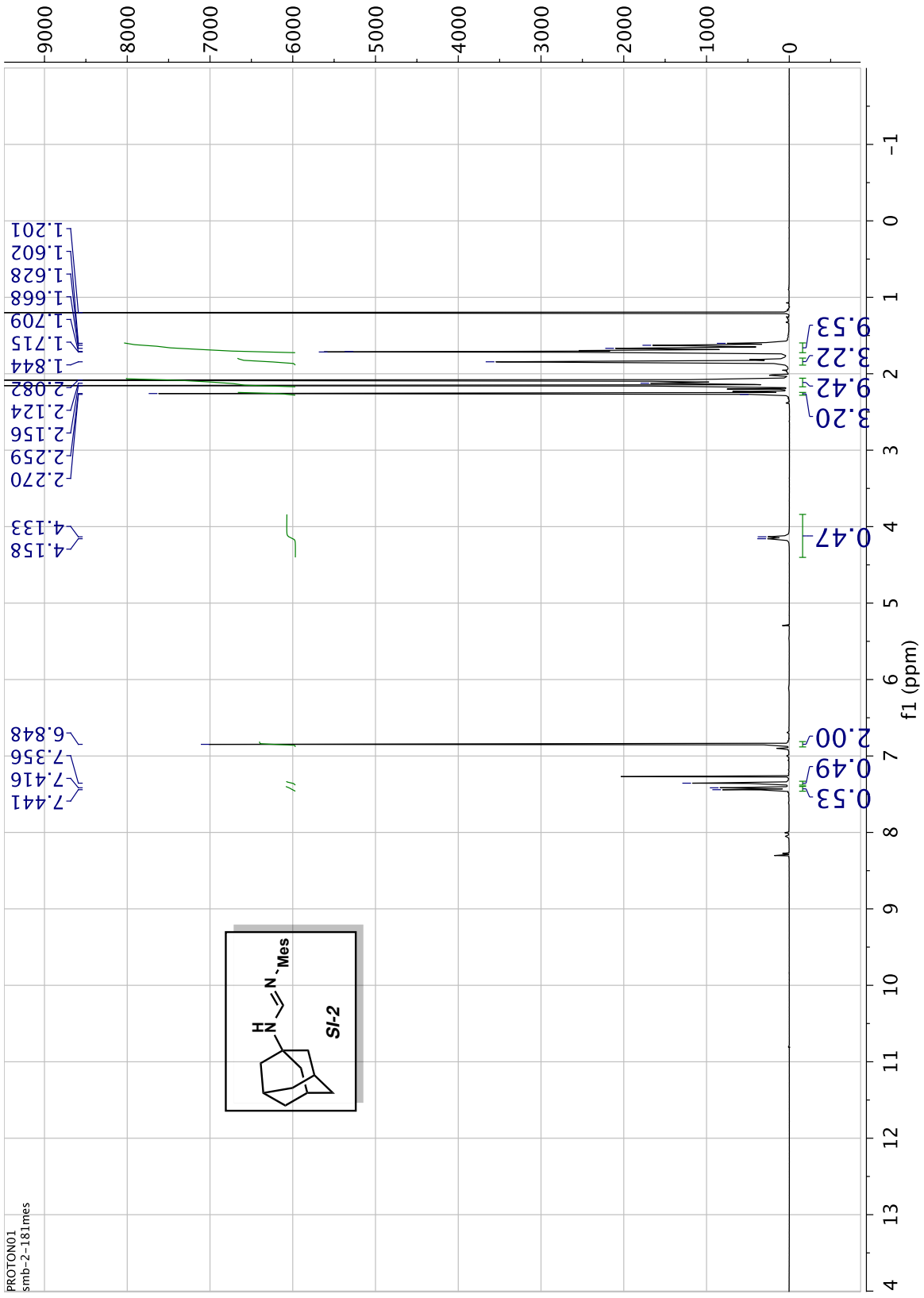


In a glovebox, a 20 mL vial was charged with vinylboronic acid pinacol ester (**36**) (135 μL, 0.800 mmol, 1.00 equiv) and 1-dodecene (**37**) (0.710 mL, 3.20 mmol, 4.00 equiv). A solution of Ru catalyst (2.0 mol%, 0.016 mmol in 0.750 mL THF) was added and the reaction was stirred open to the glovebox atmosphere at 35 °C for 5 h, after which it was removed from the glovebox. The reaction mixture was exposed to air and quenched by addition of ethyl vinyl ether (2 mL) and the solvent was removed under reduced pressure. Purification by flash chromatography (100% Pentane → 92:8 Pentane:Et_2O) provided product **38** as a clear, colorless oil. Spectra were consistent with data in previous literature reports.[12]



In a glovebox, a 4 mL vial was charged with 8-nonen-1-ol (**39**) (33.0 μL, 0.200 mmol, 1.00 equiv). Trans-1,4-hexadiene (**40**) (0.200 mL) and THF (170 μL) were added, followed by a stock solution of Ru catalyst (0.5 mol %, 0.001 mmol in 30 μL of THF). The resulting solution was stirred open to the glovebox atmosphere at room temperature for 5 h, after which it was removed from the glovebox. The reaction mixture was exposed to air and quenched by the addition of ethyl vinyl ether (1 mL) and the solvent was removed under reduced pressure. Purification by flash chromatography (Hexanes → 3:1 Hexanes:EtOAc) provided diene product **41** as a clear, colorless oil. Spectra were consistent with data in previous literature reports.[13]

^{1}H NMR Spectra: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f1 (ppm)
SI-2
Mes
0.53
0.49
2.00
0.47
3.20
9.42
3.22
9.53
7.441
7.416
7.356
6.848
4.158
4.133
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2.259
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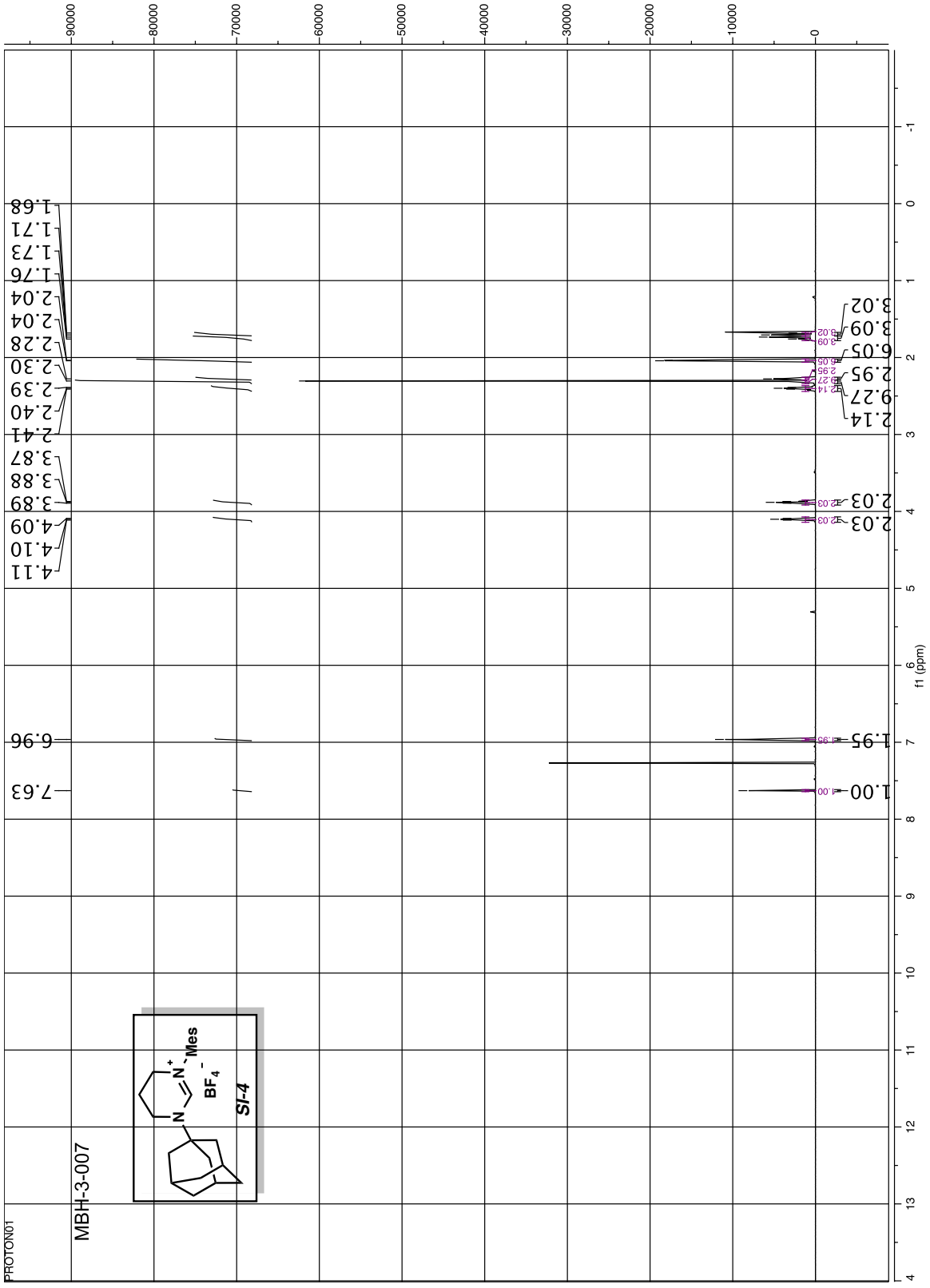
1.709
1.668
1.628
1.602
1.201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Mes
BF4
f1 (ppm)
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1.73
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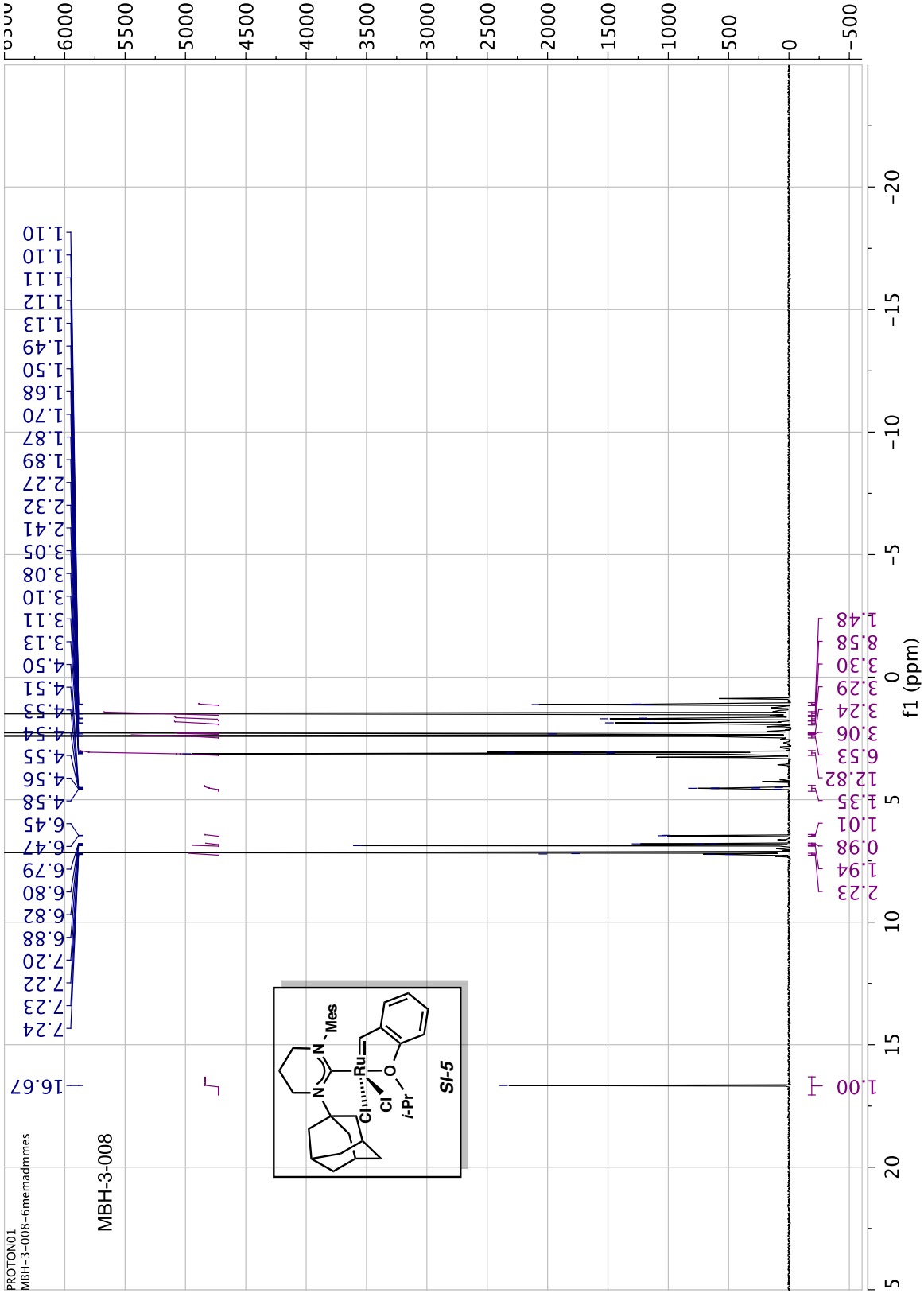
1.00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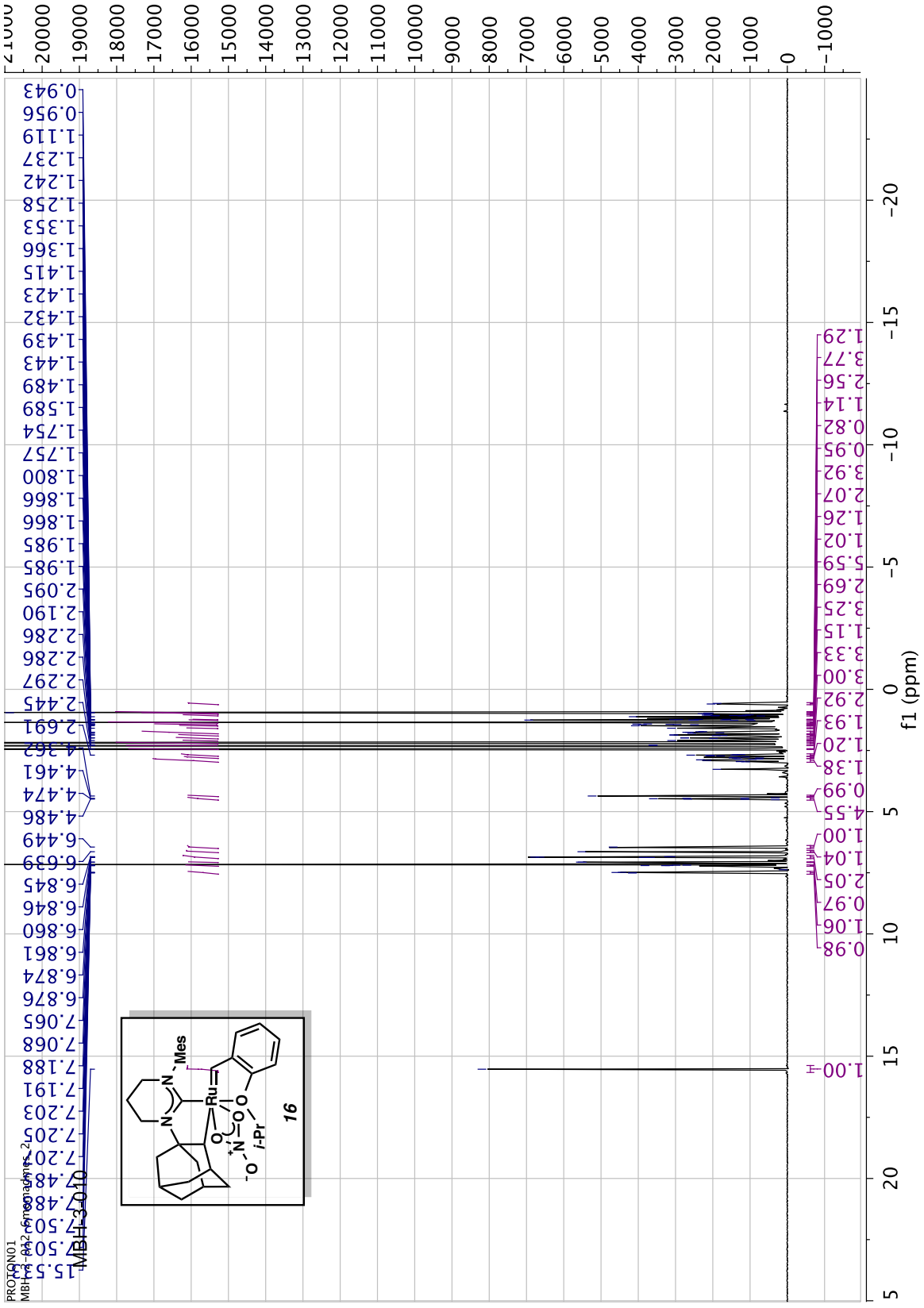
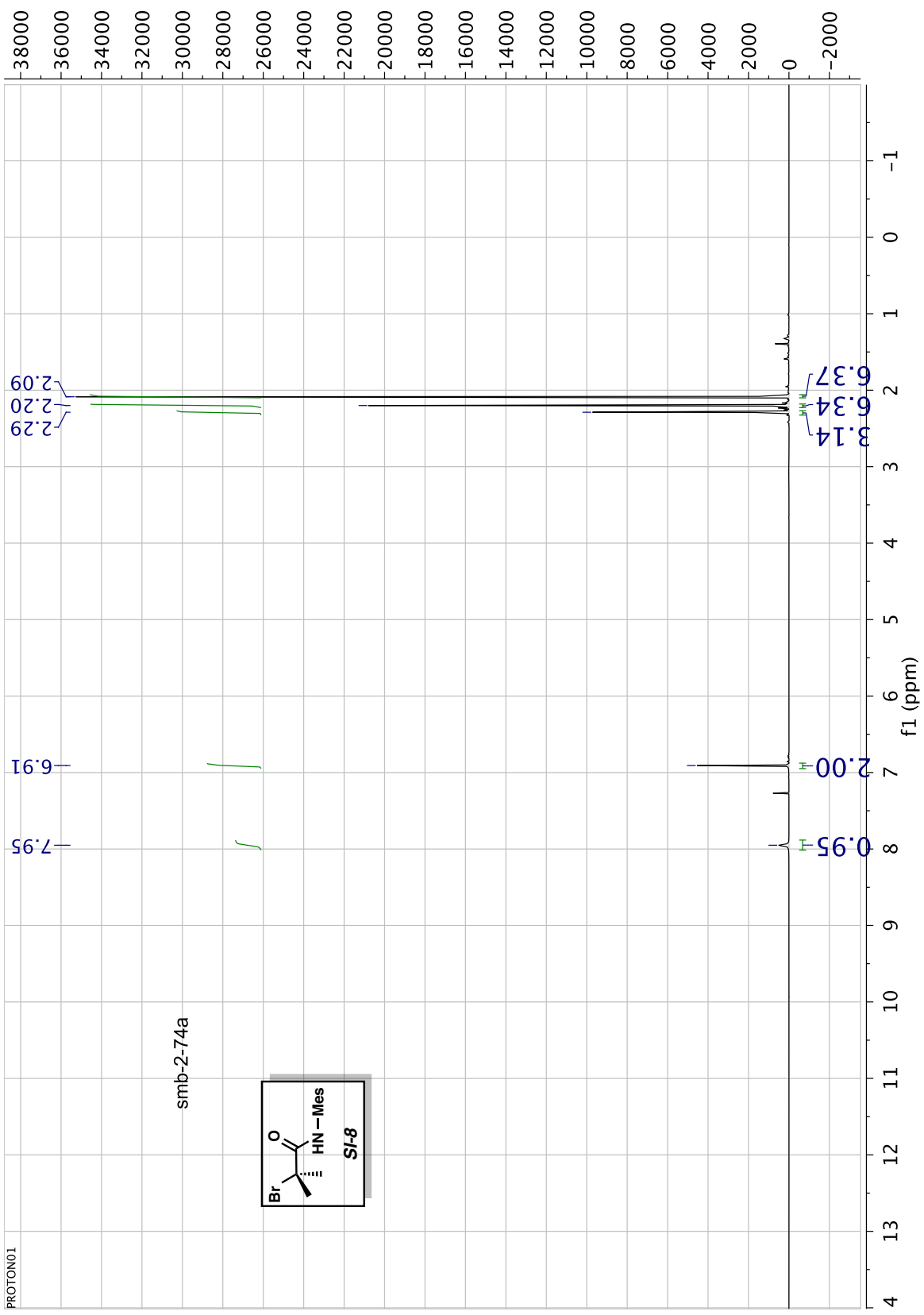
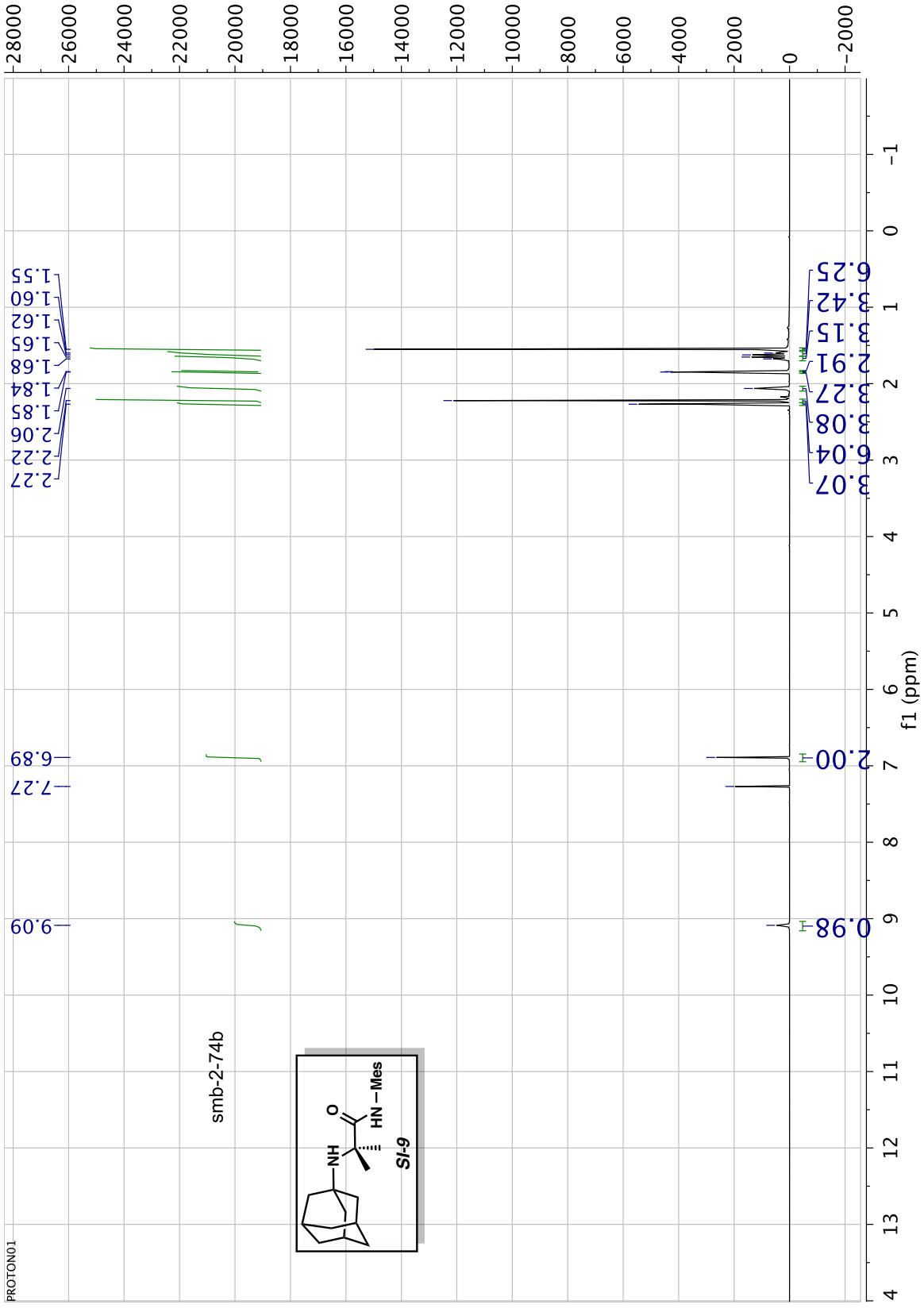
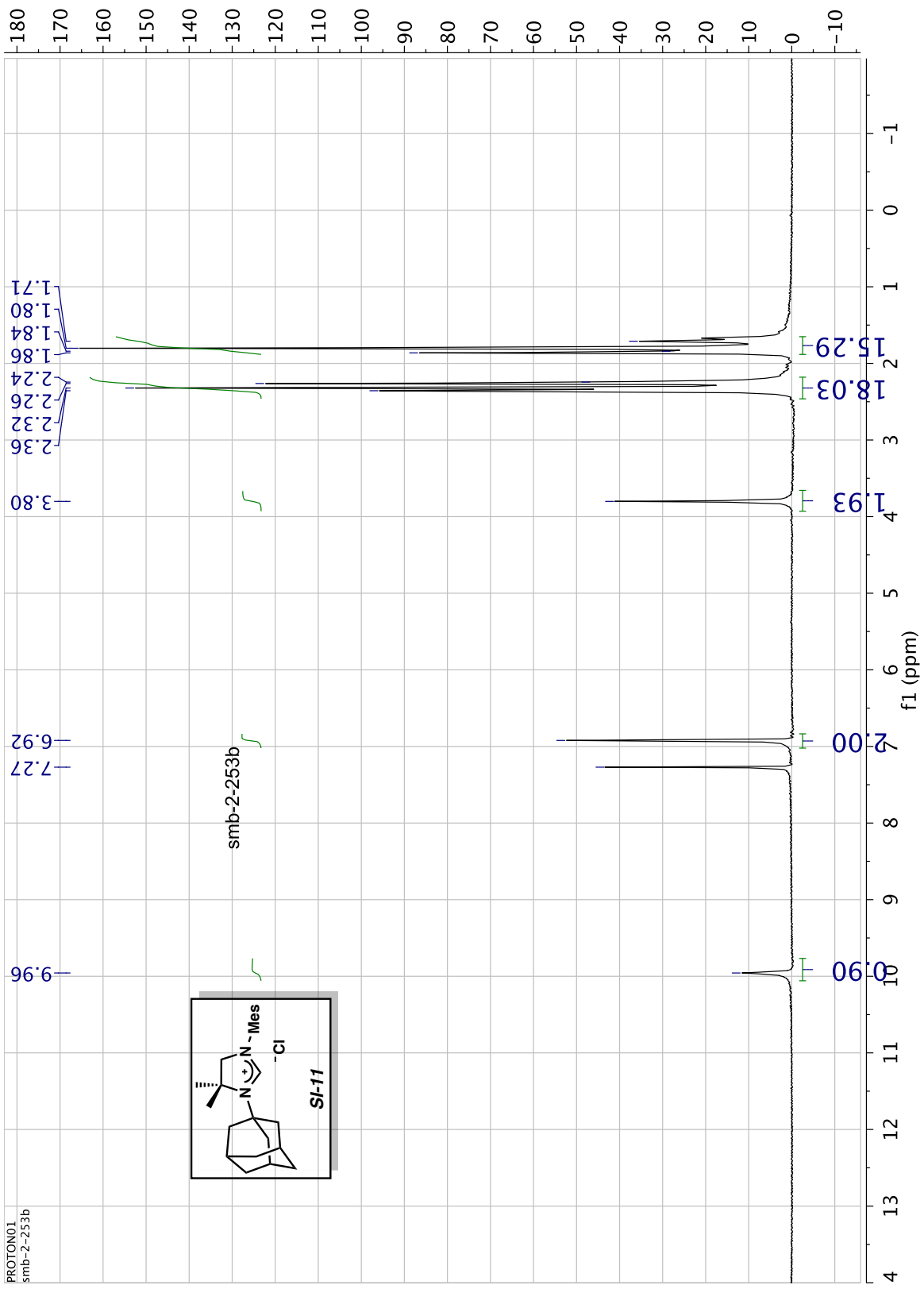
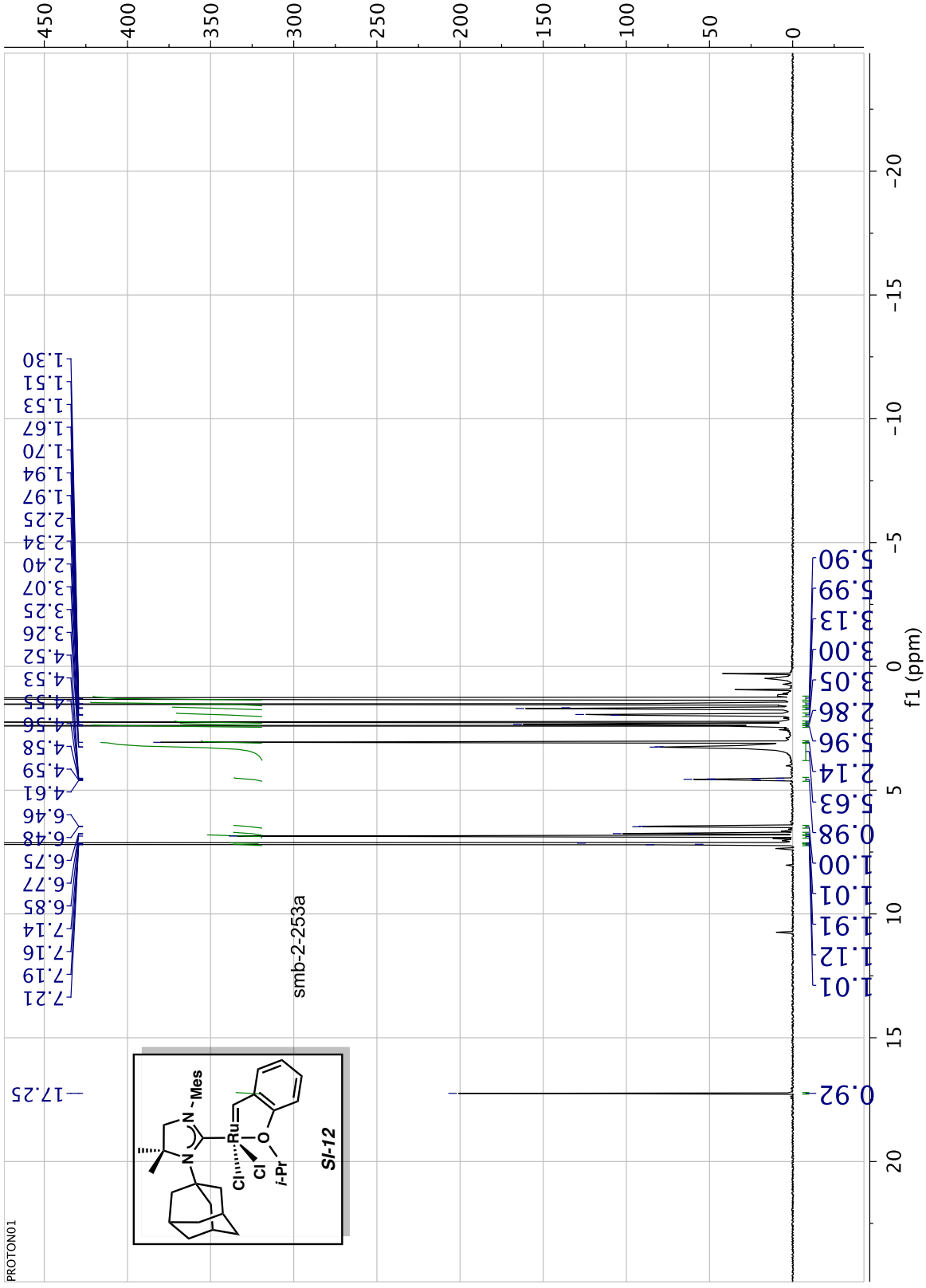
Mes
Ru
Cl
i-Pr
f1 (ppm)

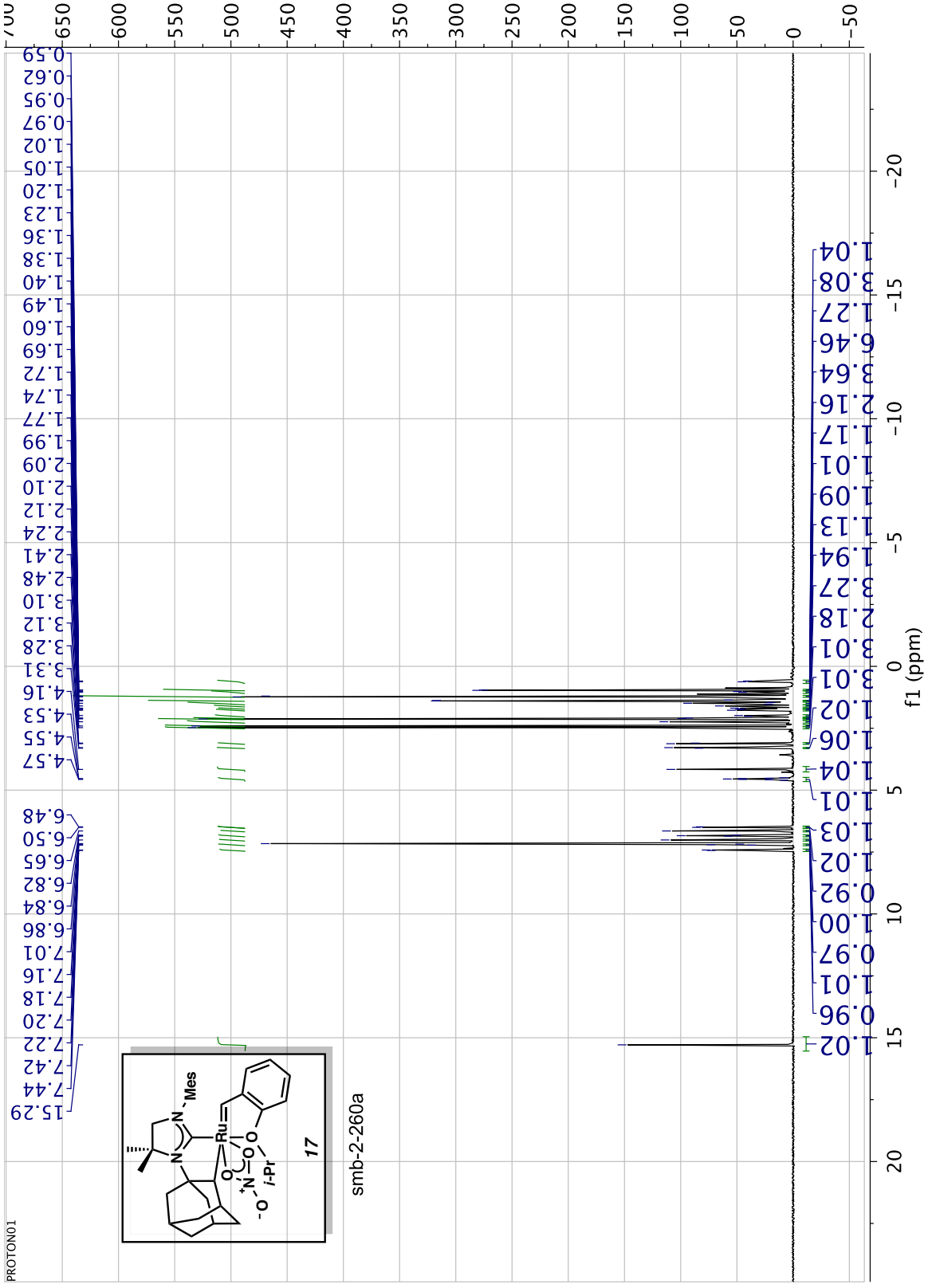

PROTON01
MBH14-042-6mmolarmix_2
MBH14-010
Mes
Ru
i-Pr
16
f1 (ppm)

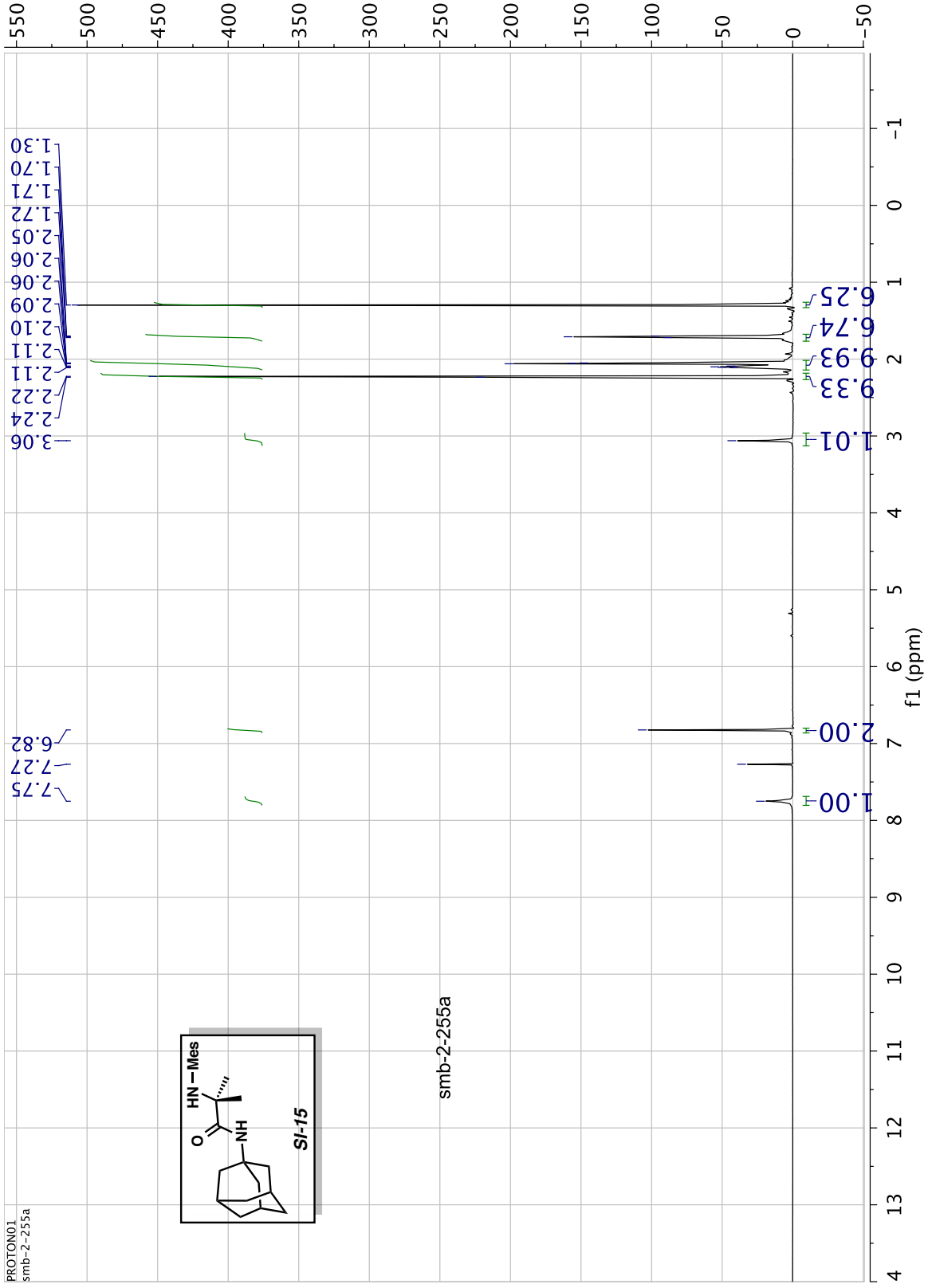

smb-2-74a
SI-8
HN – Mes
O
Br
PROTON01
f1 (ppm)
2.09
2.20
2.29
3.14
6.34
6.37
6.91
7.95
2.00
0.95

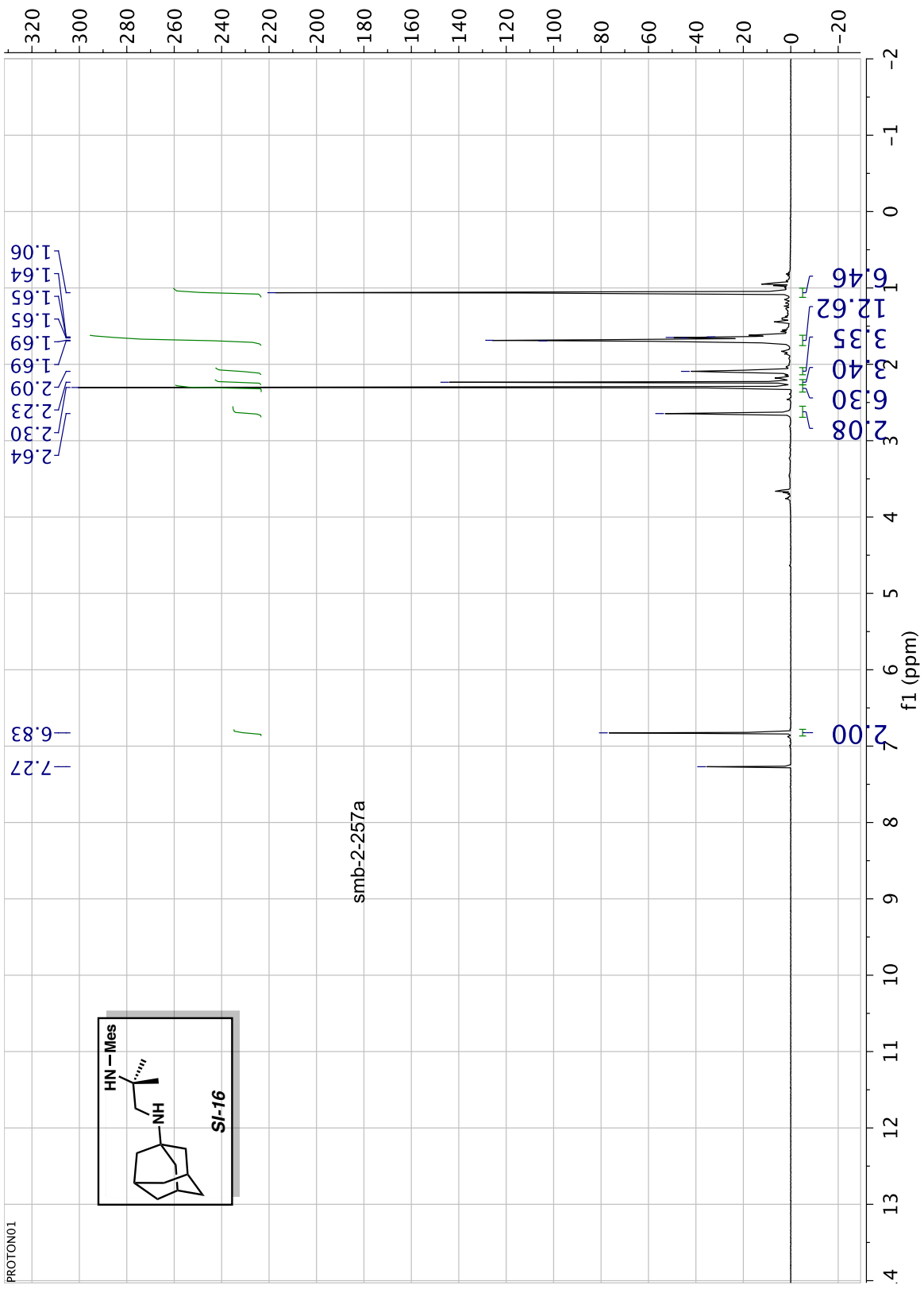

smb-2-74b
PROTON01
f1 (ppm)
Si-9
NH
O
HN—Mes
9.09
7.27
6.89
2.27
2.22
2.06
1.85
1.84
1.68
1.65
1.62
1.60
1.55
0.98
2.00
3.07
6.04
3.08
3.27
2.91
3.15
3.42
6.25

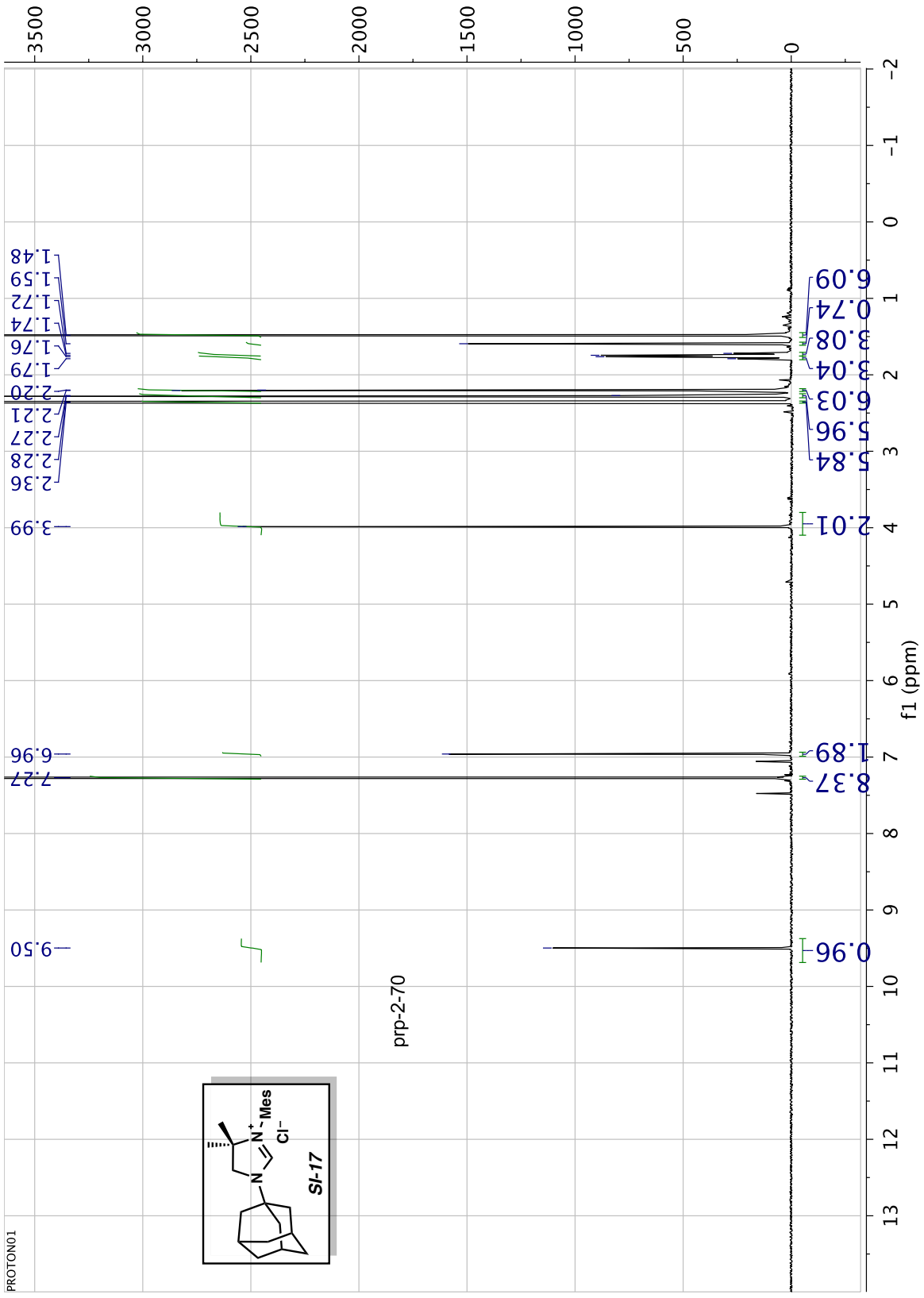

PROTON01
smb-2-253b
smb-2-253b
SI-11
N
N
Mes
Cl
9.96
7.27
6.92
3.80
2.36
2.32
2.26
2.24
1.86
1.84
1.80
1.71
0.90
2.00
1.93
18.03
15.29
f1 (ppm)

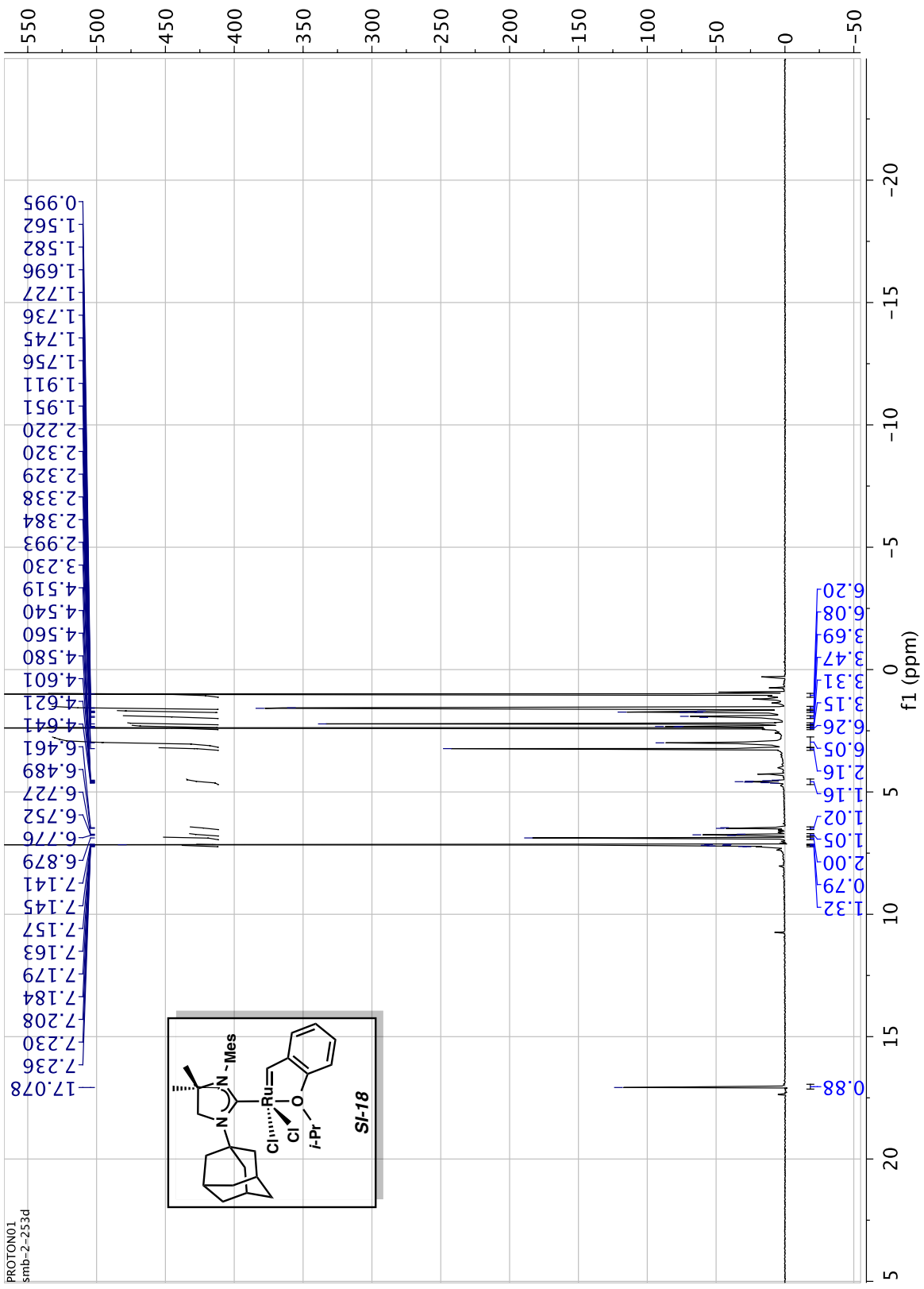

PROTON01
smb-2-253a
SI-12
Mes
i-Pr
Cl
Ru
O
N
f1 (ppm)

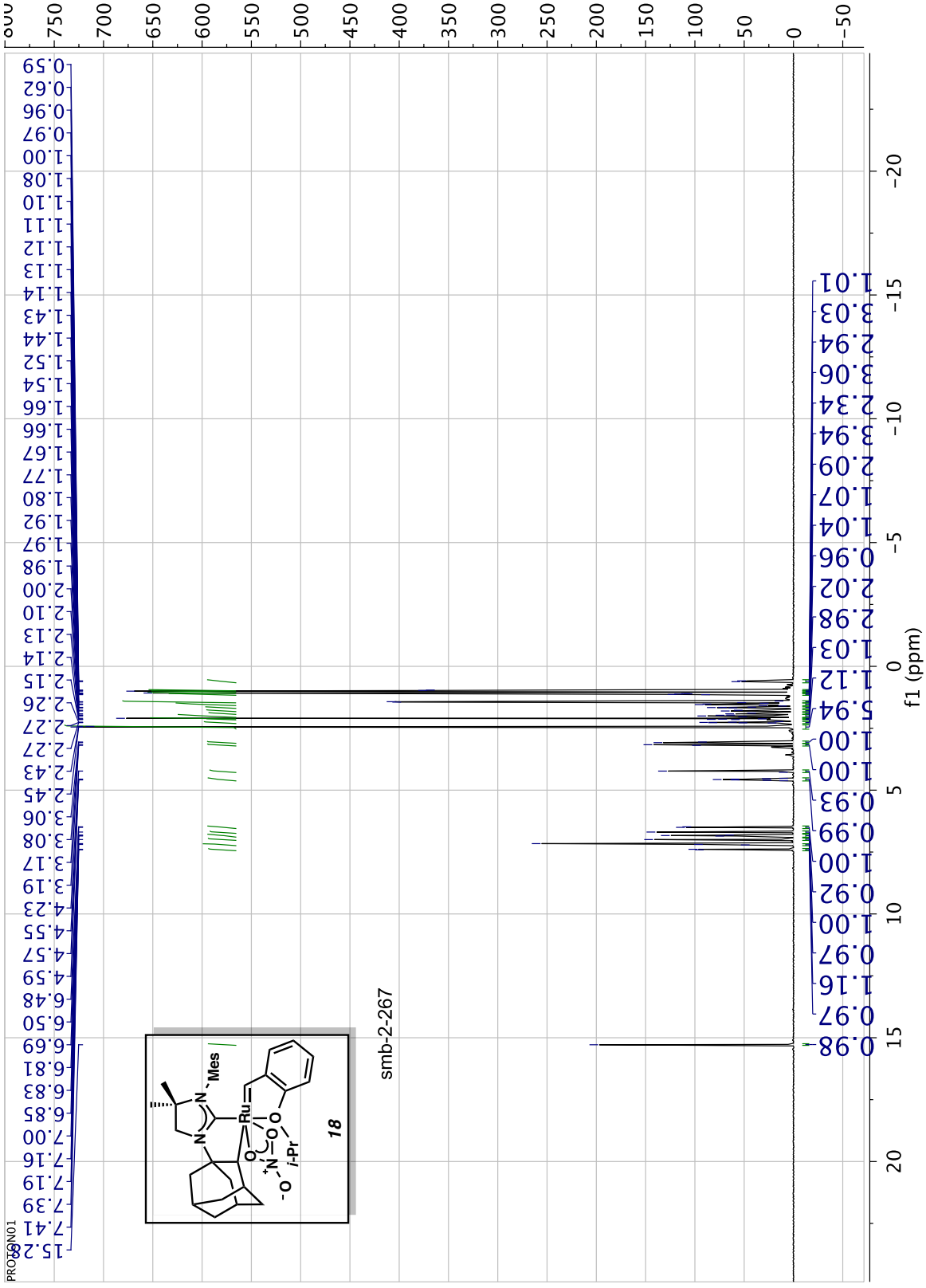

PROTON01
smb-2-260a
17
Mes
i-Pr
Ru
f1 (ppm)

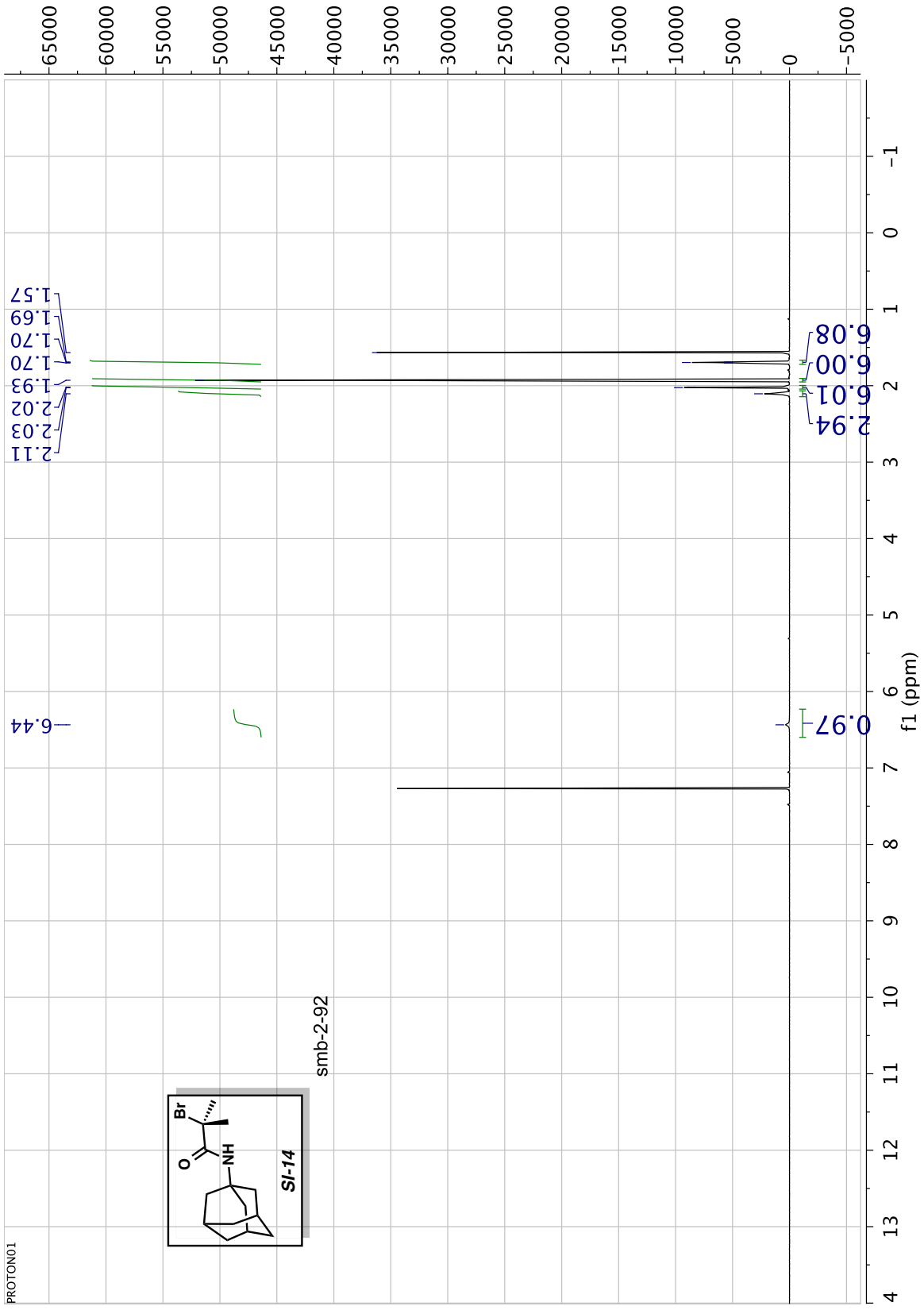

PROTON01
smb-2-255a
smb-2-255a
HN—Mes
O
NH
SI-15
f1 (ppm)
1.30
1.70
1.71
1.72
2.05
2.06
2.06
2.09
2.10
2.11
2.11
2.22
2.24
3.06
6.82
7.27
7.75
6.25
6.74
9.93
9.33
1.01
2.00
1.00

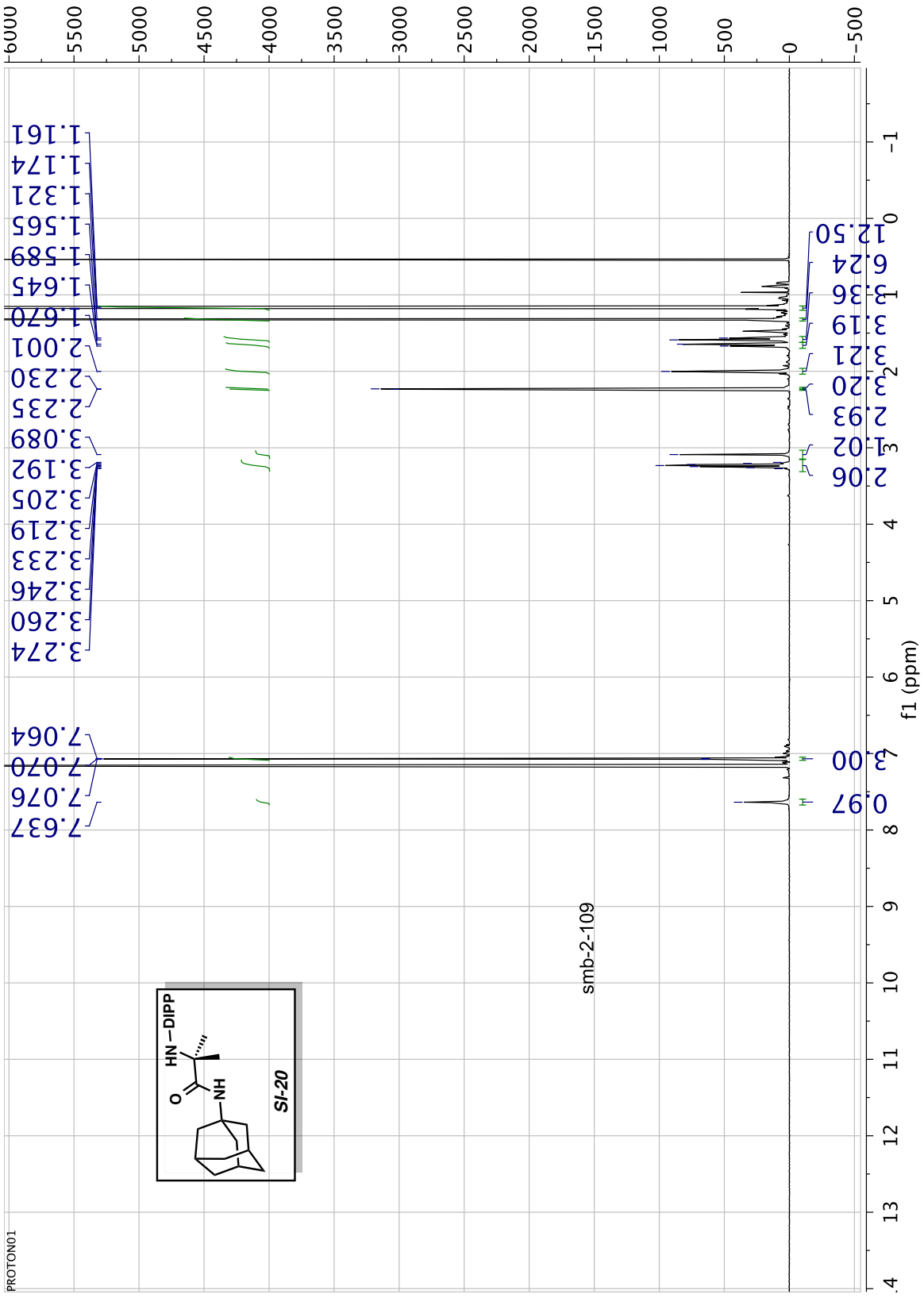

PROTON01
smb-2-257a
SI-16
HN—Mes
NH
f1 (ppm)
6.46
12.62
3.35
2.40
6.30
2.08
2.00
7.27
6.83
2.64
2.30
2.23
2.09
1.69
1.69
1.65
1.65
1.64
1.06

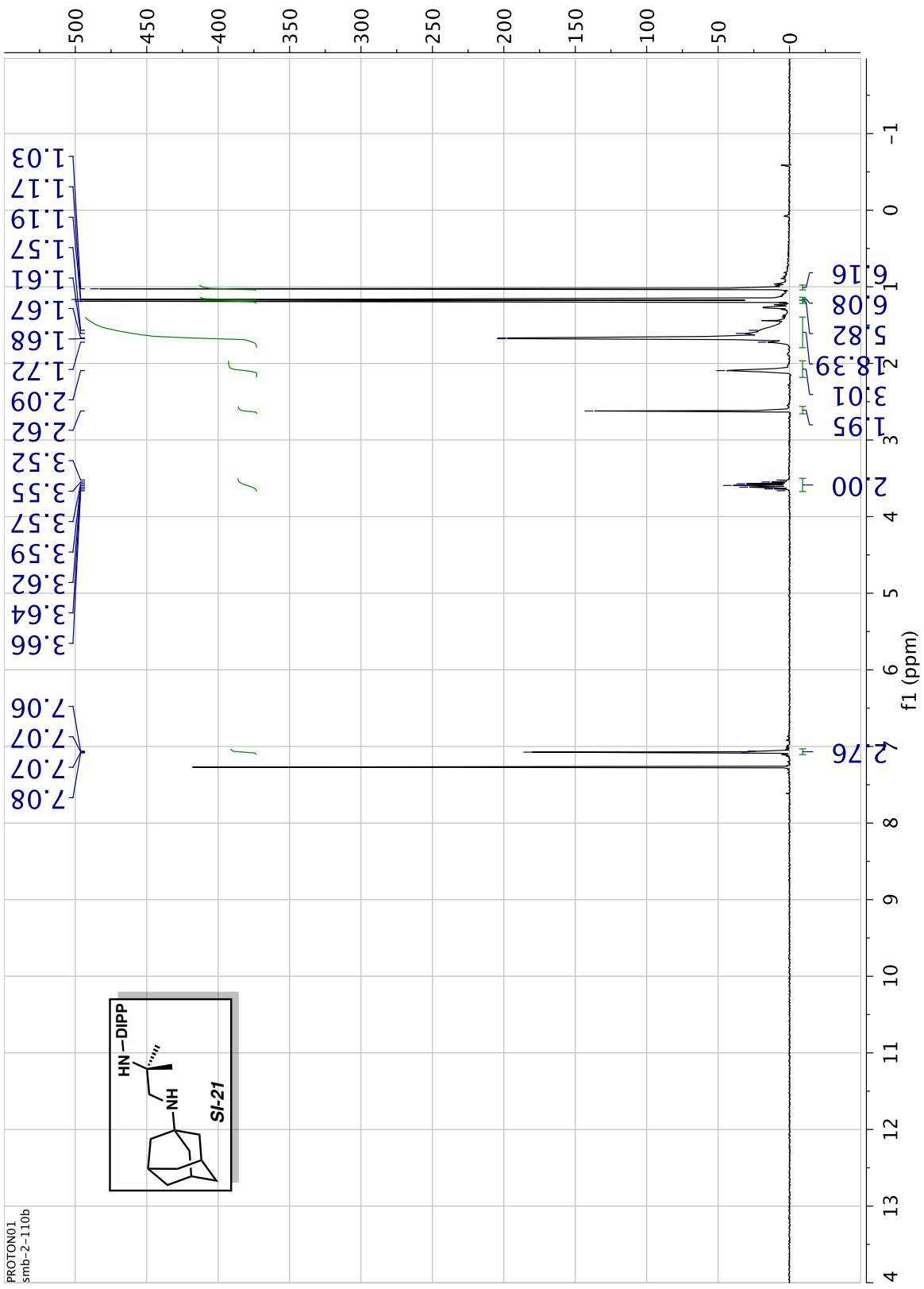

PROTON01
prp-2-70
SI-17
Mes
Cl⁻
f1 (ppm)
9.50
7.27
6.96
3.99
2.36
2.28
2.27
2.21
2.20
1.79
1.76
1.74
1.72
1.59
1.48
6.09
0.74
3.08
3.04
6.03
5.96
5.84
2.01
1.89
8.37
0.96

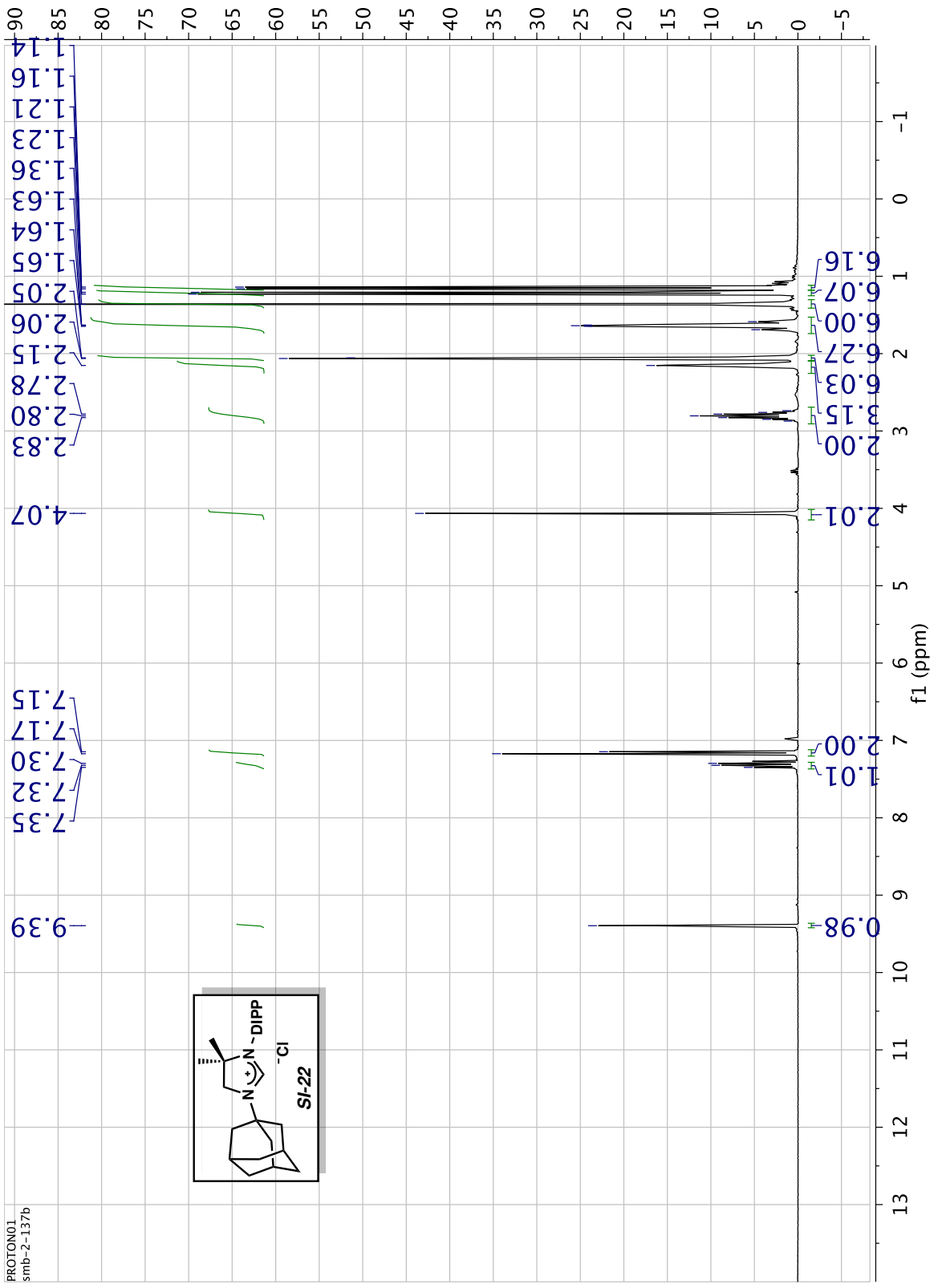

f1 (ppm)
PROTON01
smb-2-253d
SI-18
Mes
Ru
Cl
i-Pr

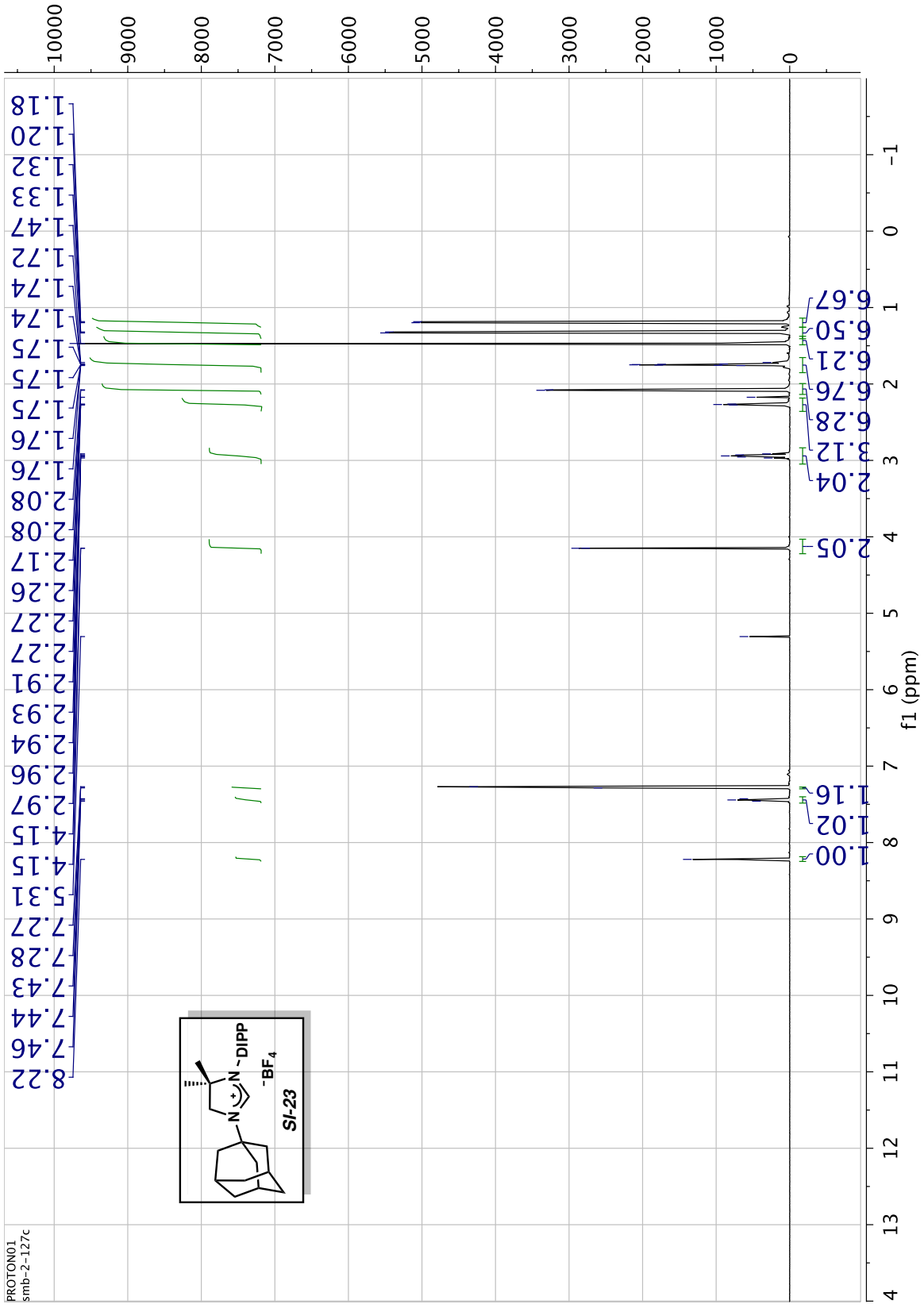

PROTON01
smb-2-267
f1 (ppm)
18
Mes
Ru
i-Pr

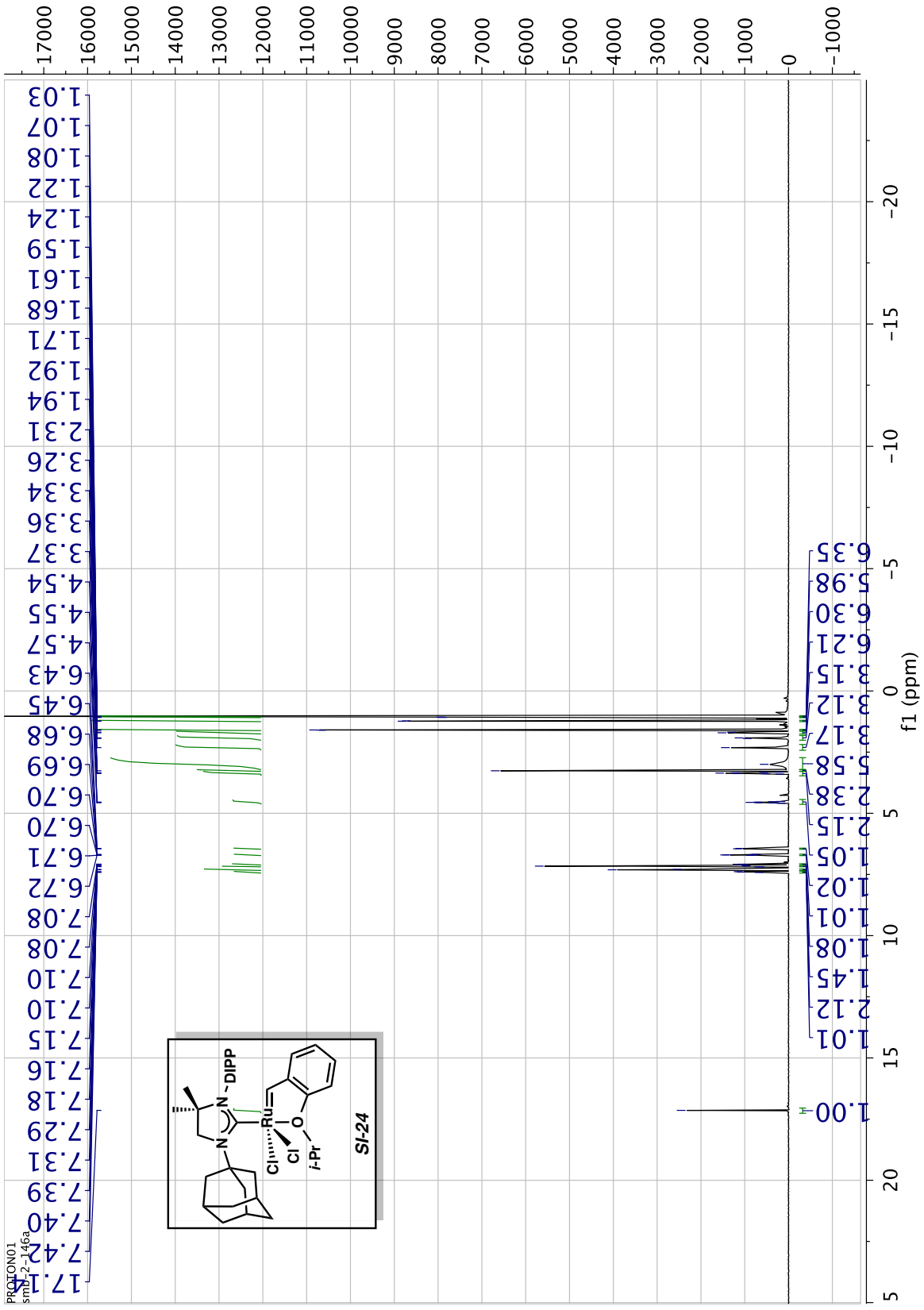

PROTON01
smb-2-92
SI-14
Br
O
NH
f1 (ppm)
2.94
6.01
6.00
6.08
0.97
6.44
2.11
2.03
2.02
1.93
1.70
1.70
1.69
1.57

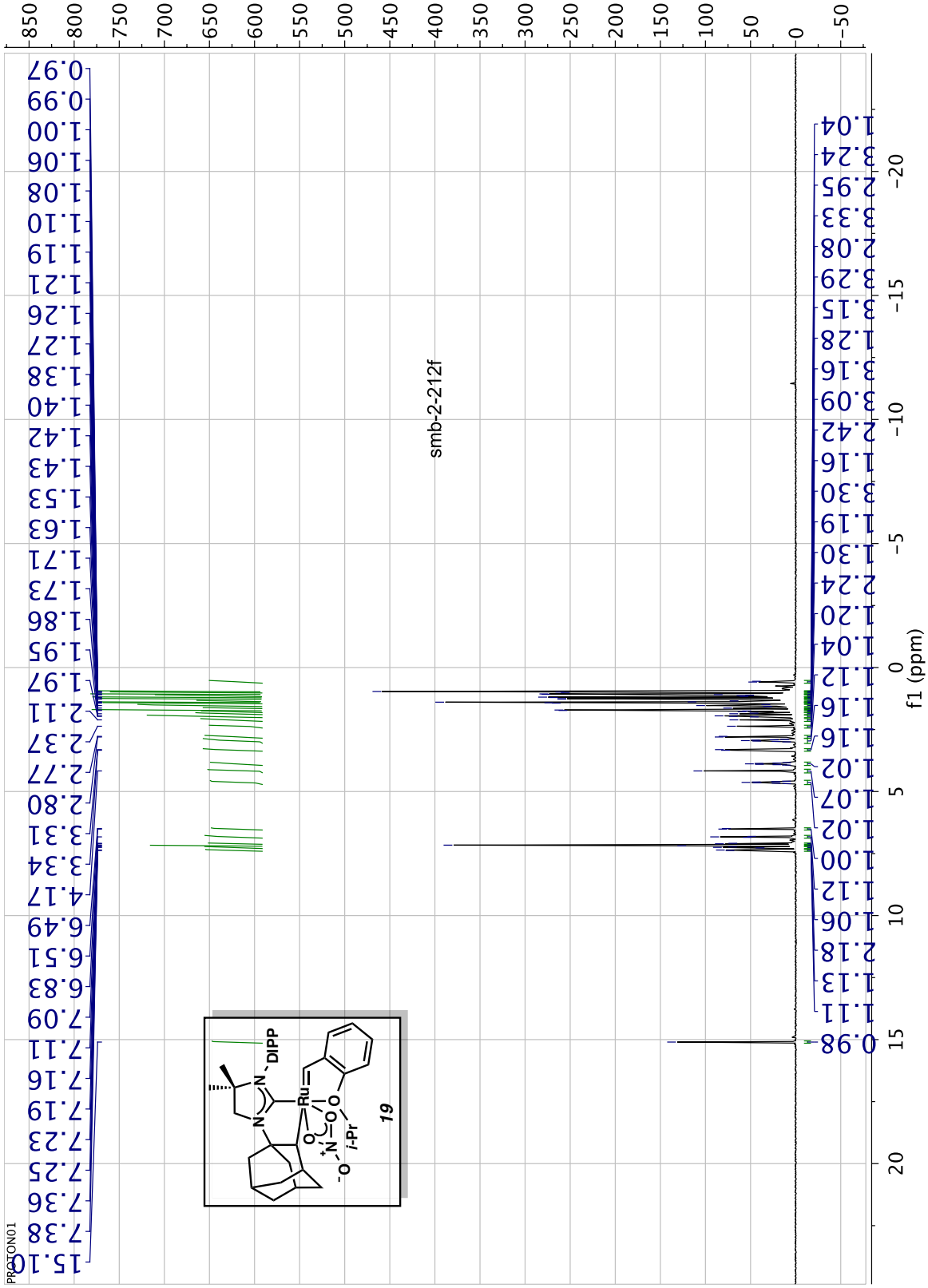

PROTON01
smb-2-109
SI-20
HN—DIPP
NH
O
f1 (ppm)
7.637
7.076
7.070
7.064
3.274
3.260
3.246
3.233
3.219
3.205
3.192
3.089
2.235
2.230
2.001
1.670
1.645
1.589
1.565
1.321
1.174
1.161
12.50
6.24
3.36
3.19
3.21
3.20
2.93
1.02
2.06
3.00
0.97

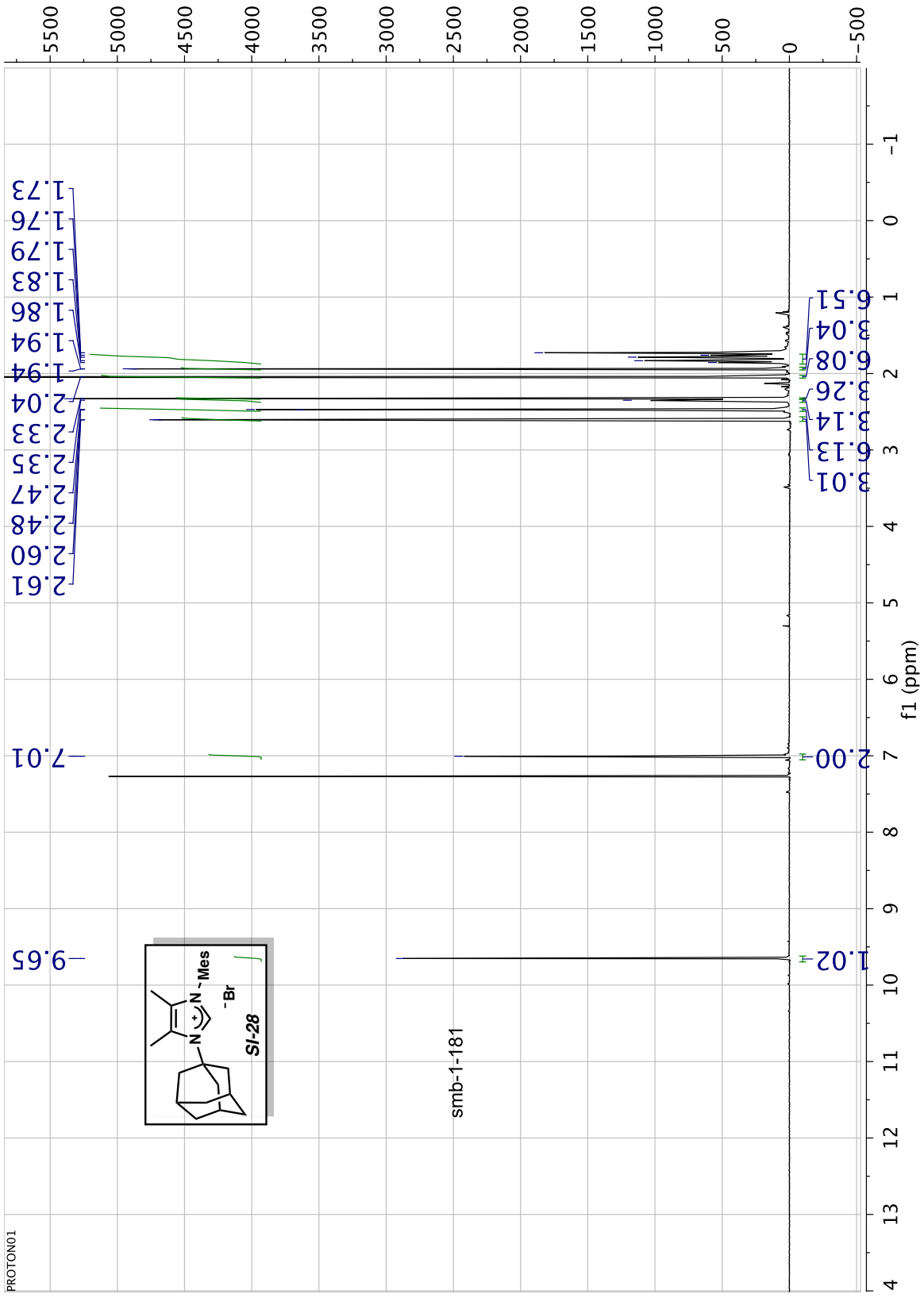

PROTON01
smb-2-110b
HN—DIPP
NH
SI-21
f1 (ppm)
7.08
7.07
7.07
7.06
3.66
3.64
3.62
3.59
3.57
3.55
3.52
2.62
2.09
1.72
1.68
1.67
1.61
1.57
1.19
1.17
1.03
6.16
6.08
5.82
18.39
3.01
1.95
2.00
2.76

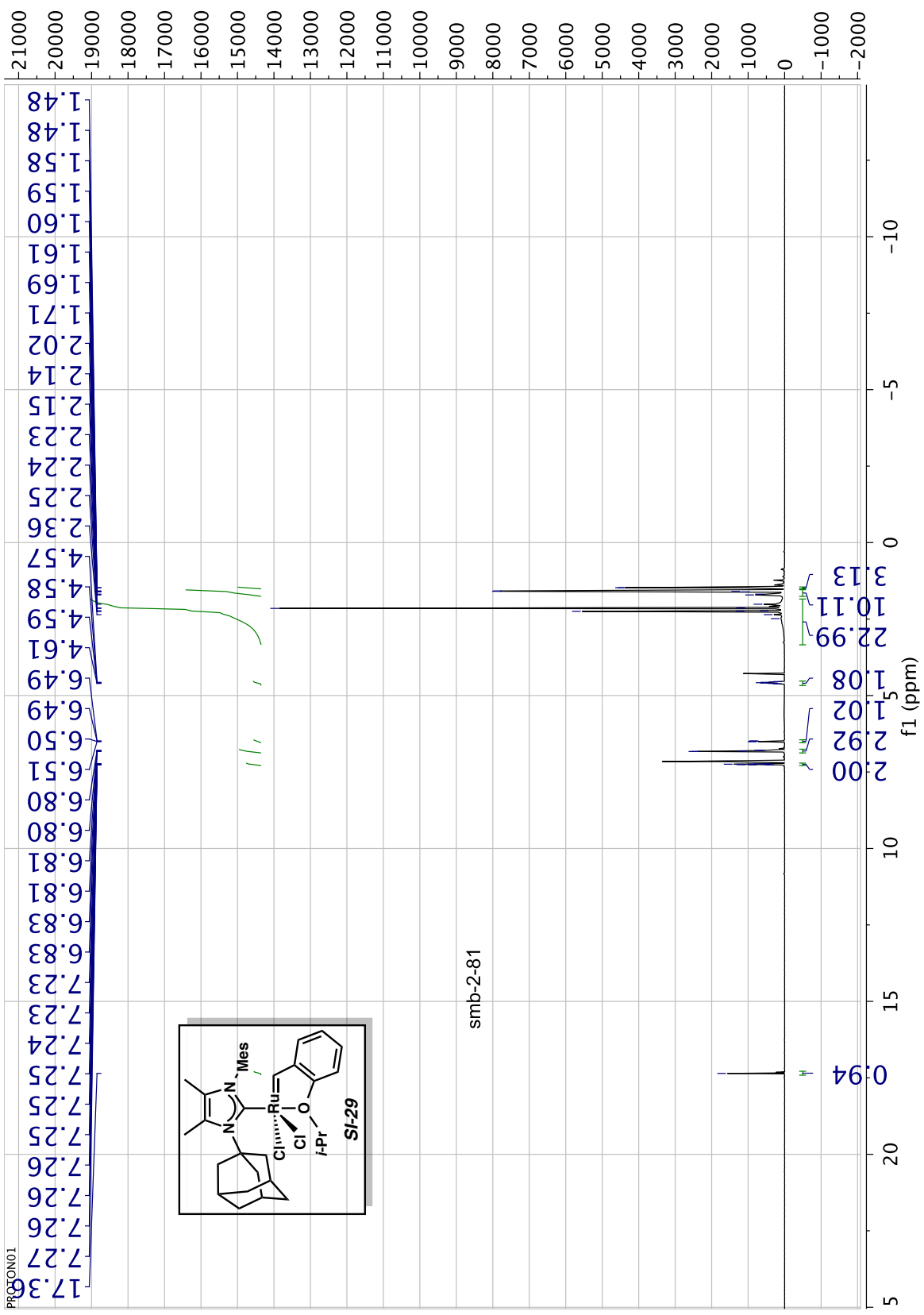

PROTON01
smb-2-137b
f1 (ppm)
SI-22
DIPP
Cl
9.39
7.35
7.32
7.30
7.17
7.15
4.07
2.83
2.80
2.78
2.15
2.06
2.05
1.65
1.64
1.63
1.36
1.23
1.21
1.16
1.14
0.98
2.00
1.01
2.01
2.00
3.15
6.03
6.27
6.00
6.07
6.16

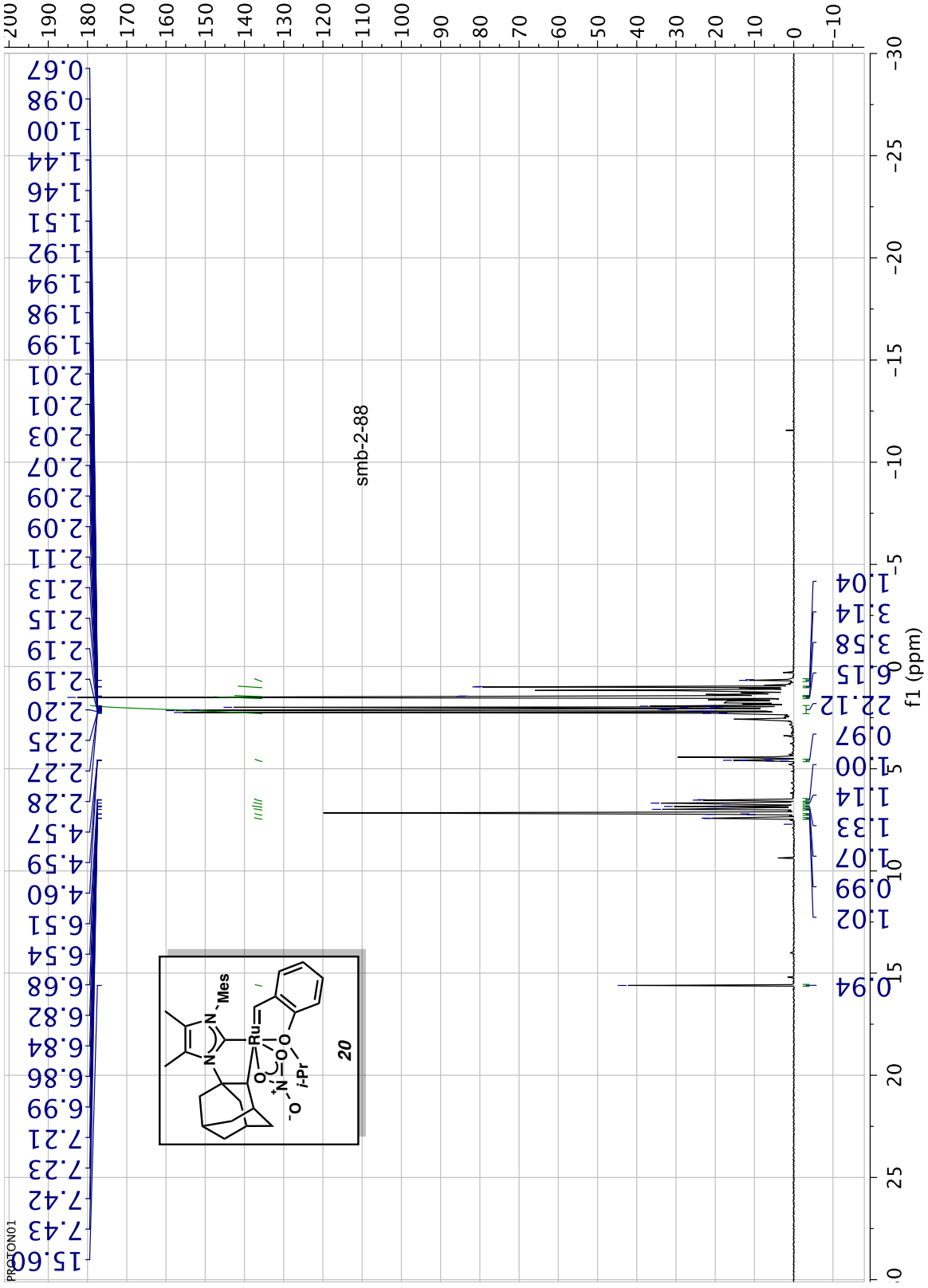

PROTON01
smb-2-127c
f1 (ppm)
SI-23
DIPP
BF4
1.00
1.02
1.16
2.04
2.05
3.12
6.21
6.28
6.50
6.67
6.76
1.18
1.20
1.32
1.33
1.47
1.72
1.74
1.74
1.75
1.75
1.75
1.76
1.76
2.08
2.08
2.17
2.26
2.27
2.27
2.91
2.93
2.94
2.96
2.97
4.15
4.15
5.31
7.27
7.28
7.43
7.44
7.46
8.22

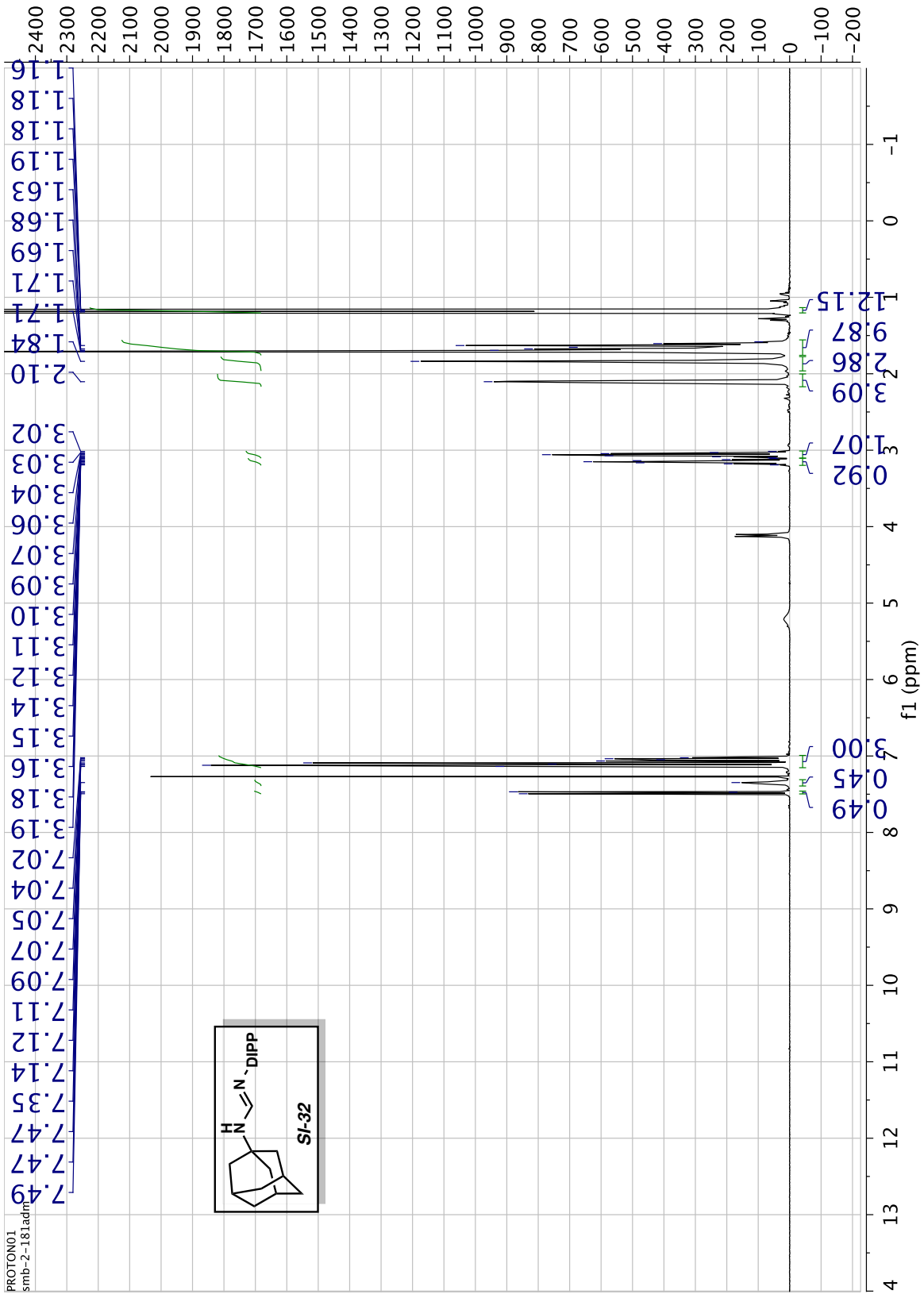

PROTON01
smb2-146a
f1 (ppm)
DIPP
Ru
Cl
O
i-Pr
SI-24

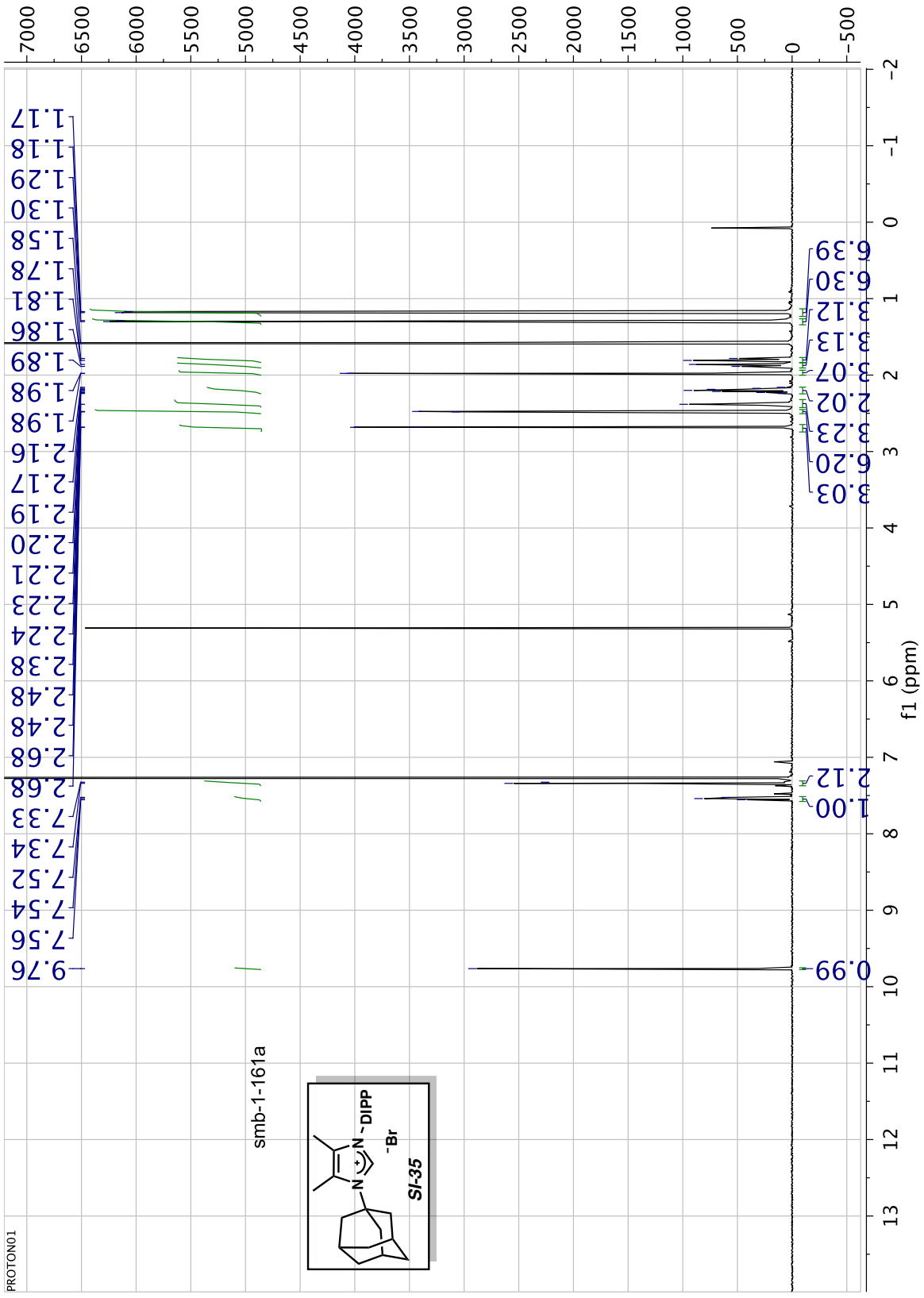

PROTON01
smb-2-212f
f1 (ppm)
DIPP
Ru
i-Pr
19

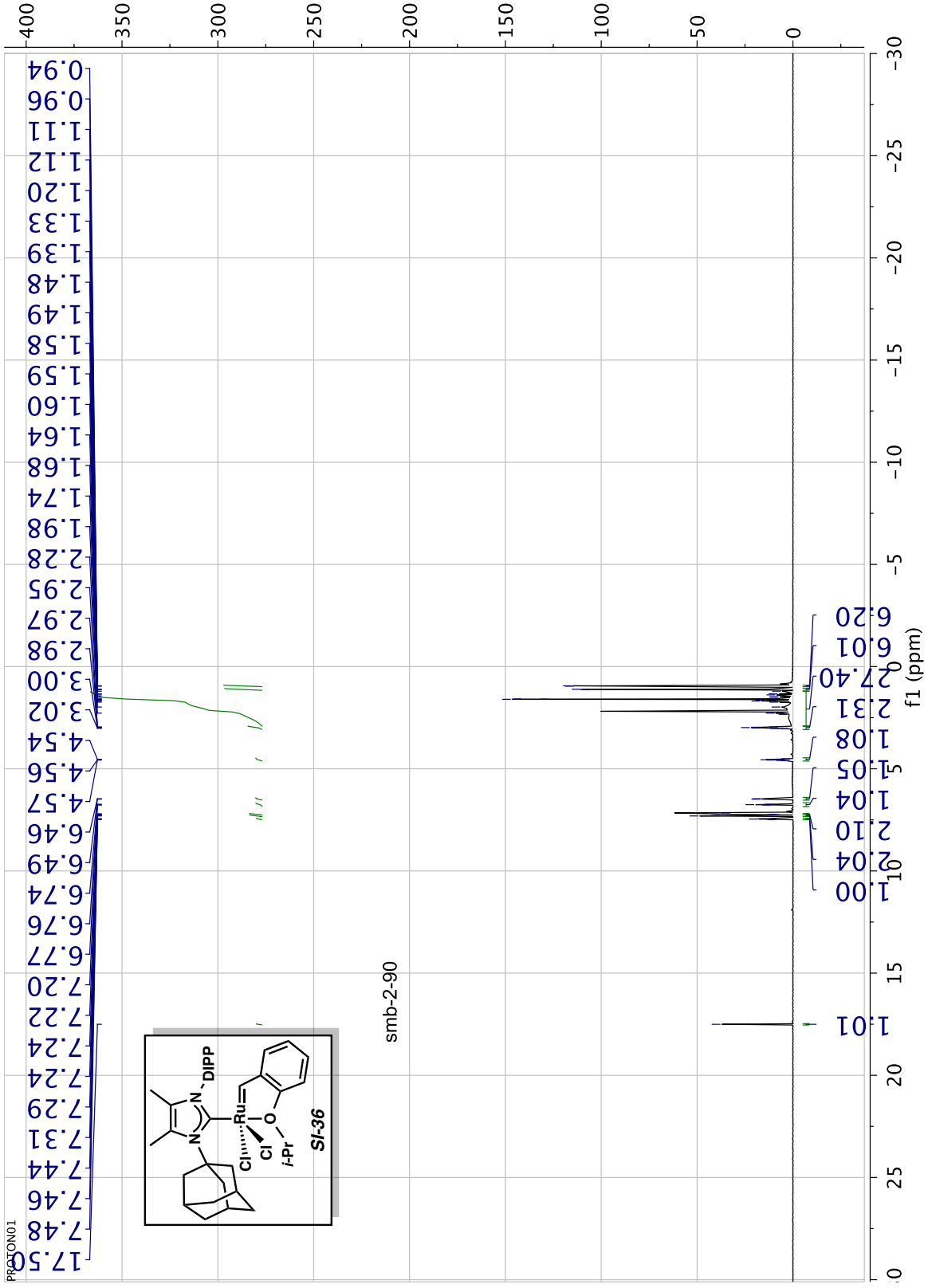

PROTON01
smb-1-181
SI-28
Mes
Br
f1 (ppm)
9.65
7.01
2.00
1.02
6.51
3.04
6.08
3.26
3.14
6.13
3.01
1.94
1.86
1.83
1.79
1.76
1.73
2.61
2.60
2.48
2.47
2.35
2.33
2.04

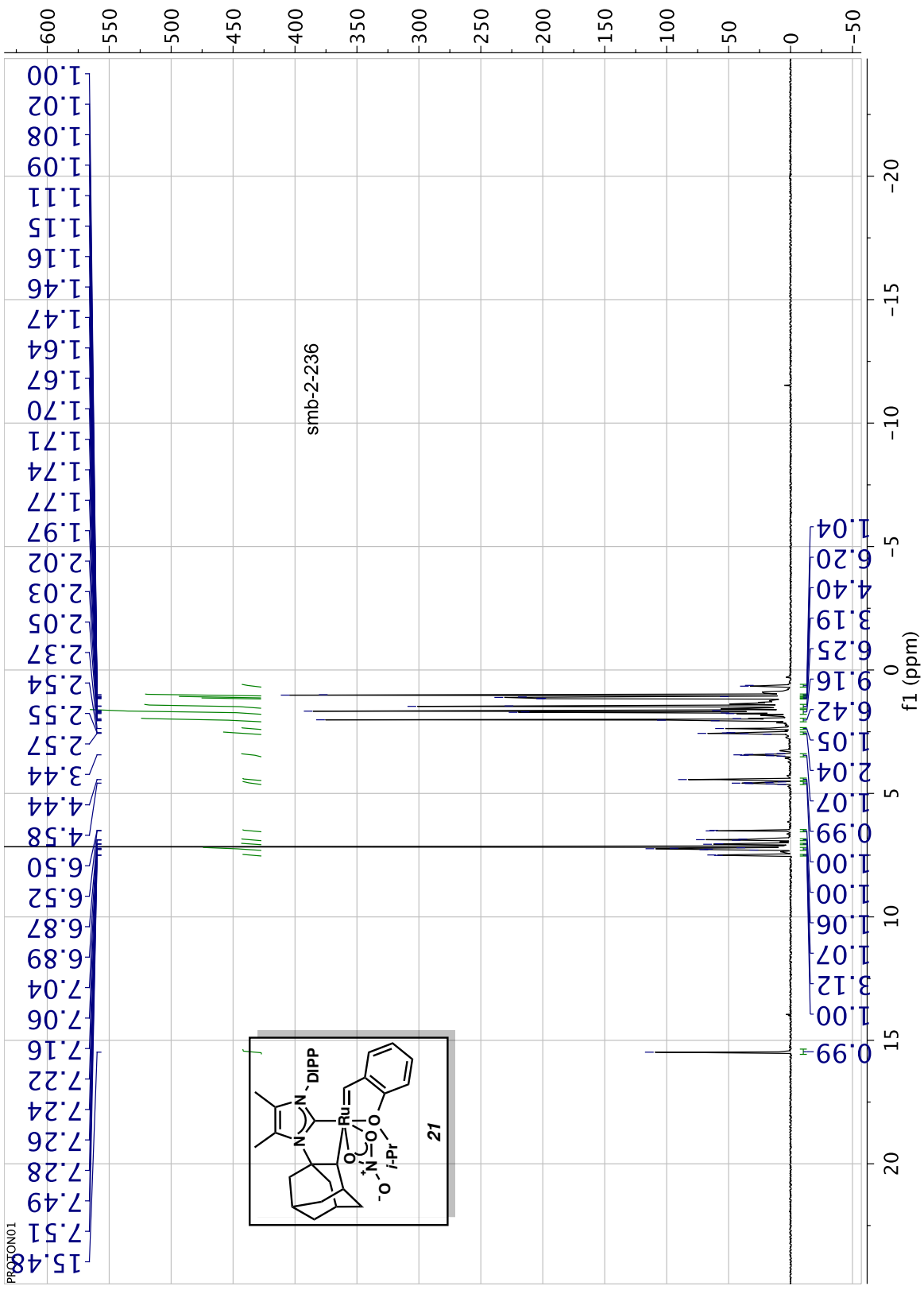

PROTON01
smb-2-81
f1 (ppm)
Mes
Ru
Cl
i-Pr
SI-29

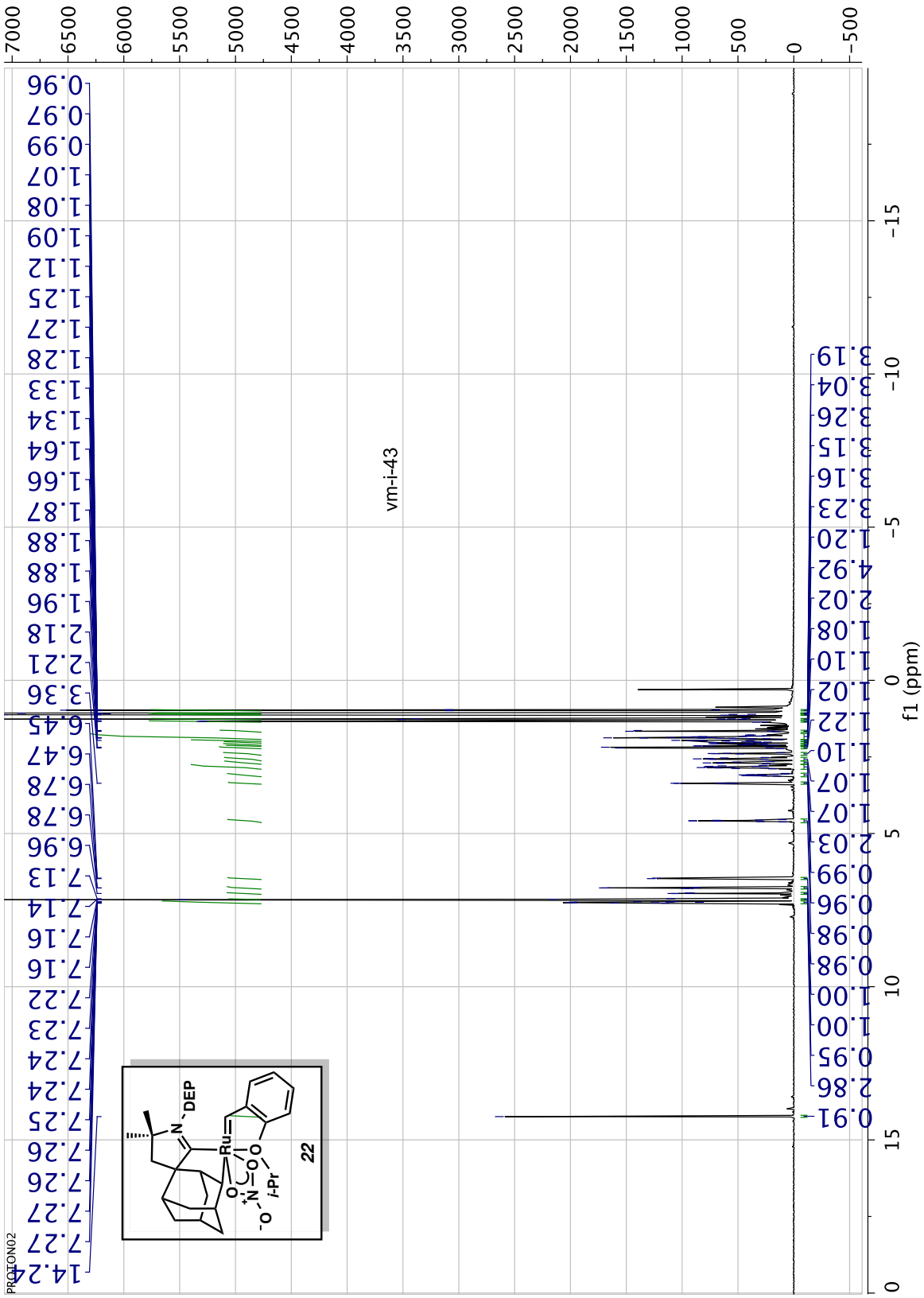

smb-2-88
PROTON01
f1 (ppm)
Mes
Ru
i-Pr
20

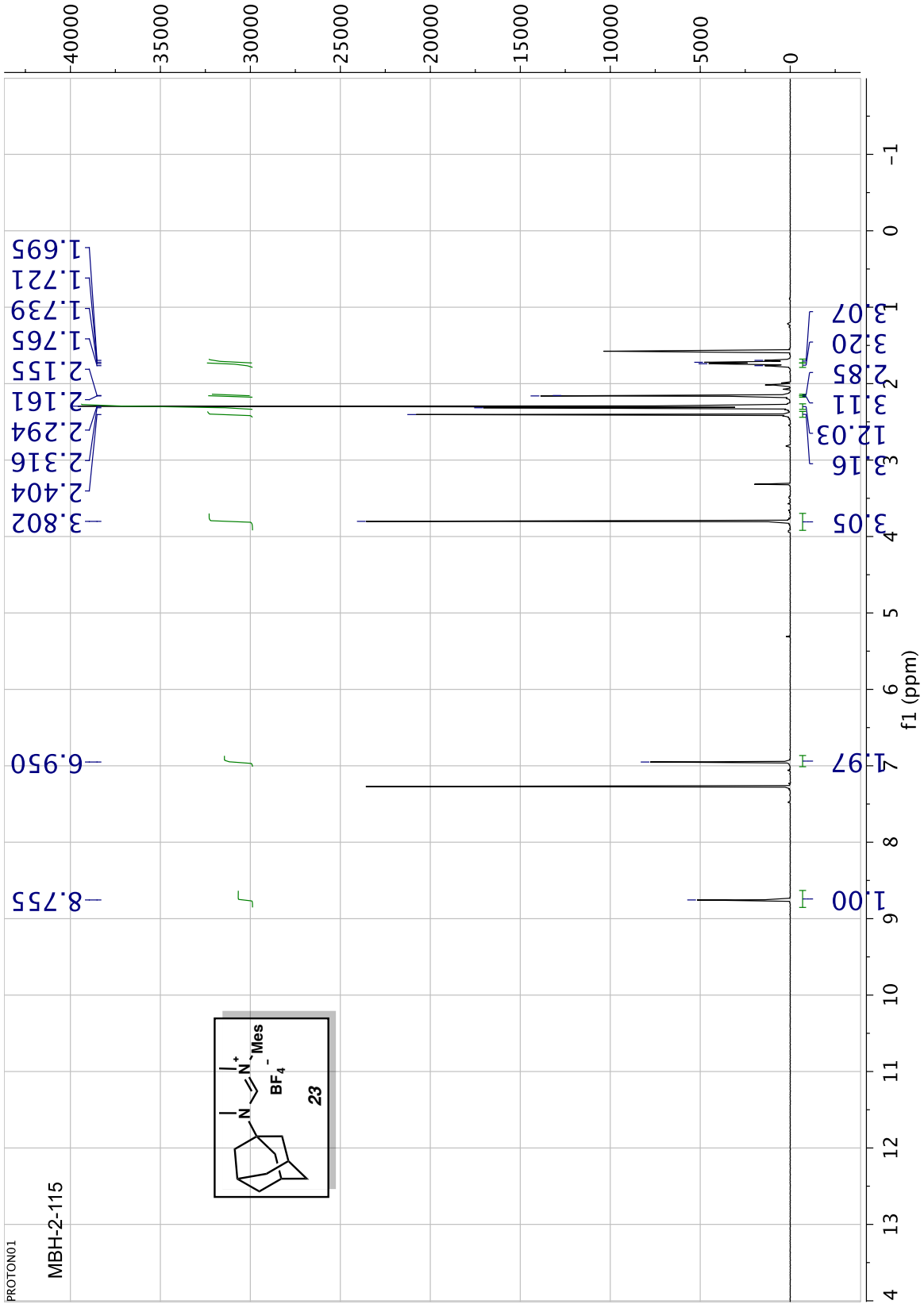

PROTON01
smb-2-181adm
f1 (ppm)
SI-32
DIPP
12.15
9.87
2.86
3.09
1.07
0.92
3.00
0.45
0.49

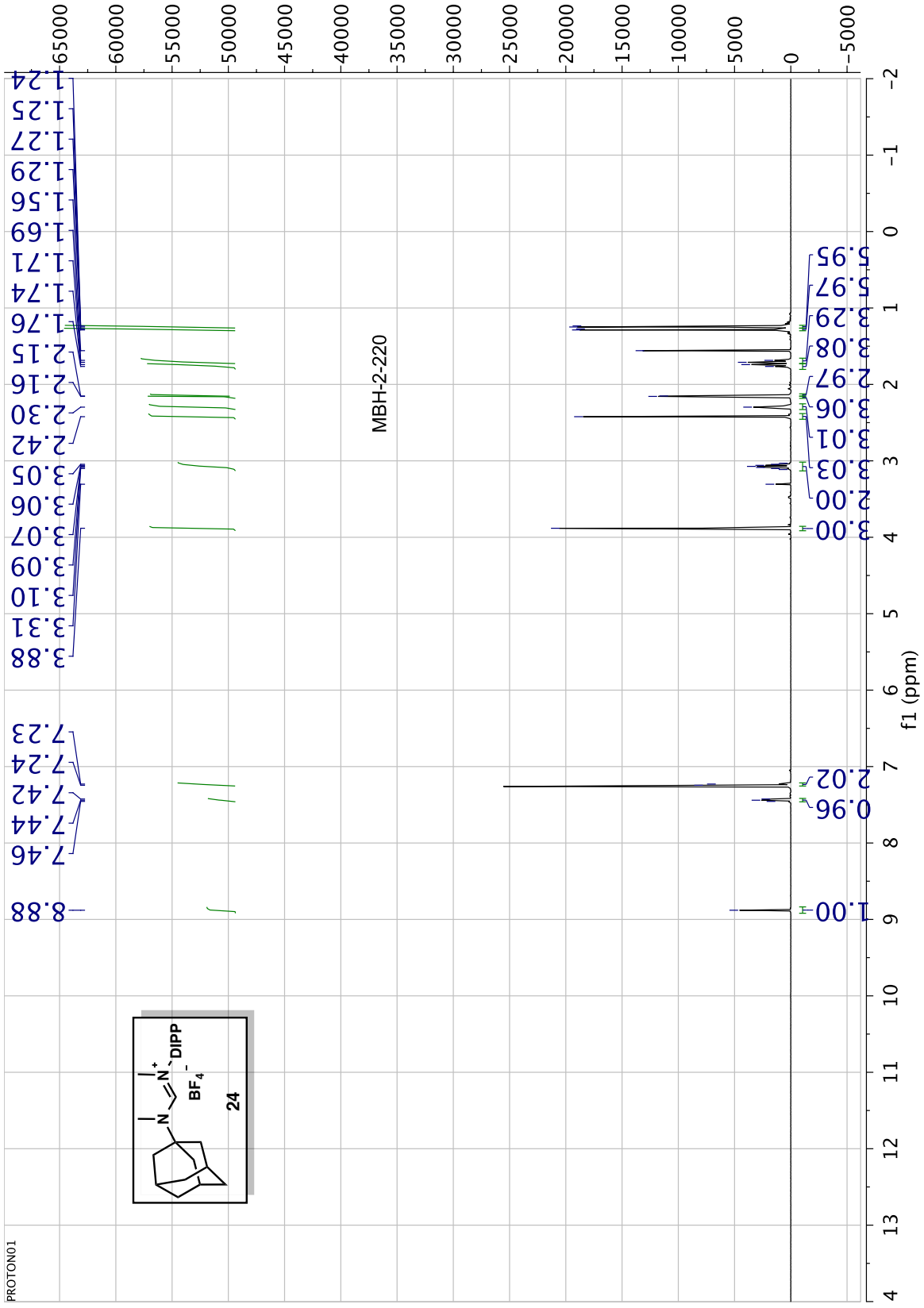

smb-1-161a
SI-35
DIPP
Br
PROTON01
f1 (ppm)

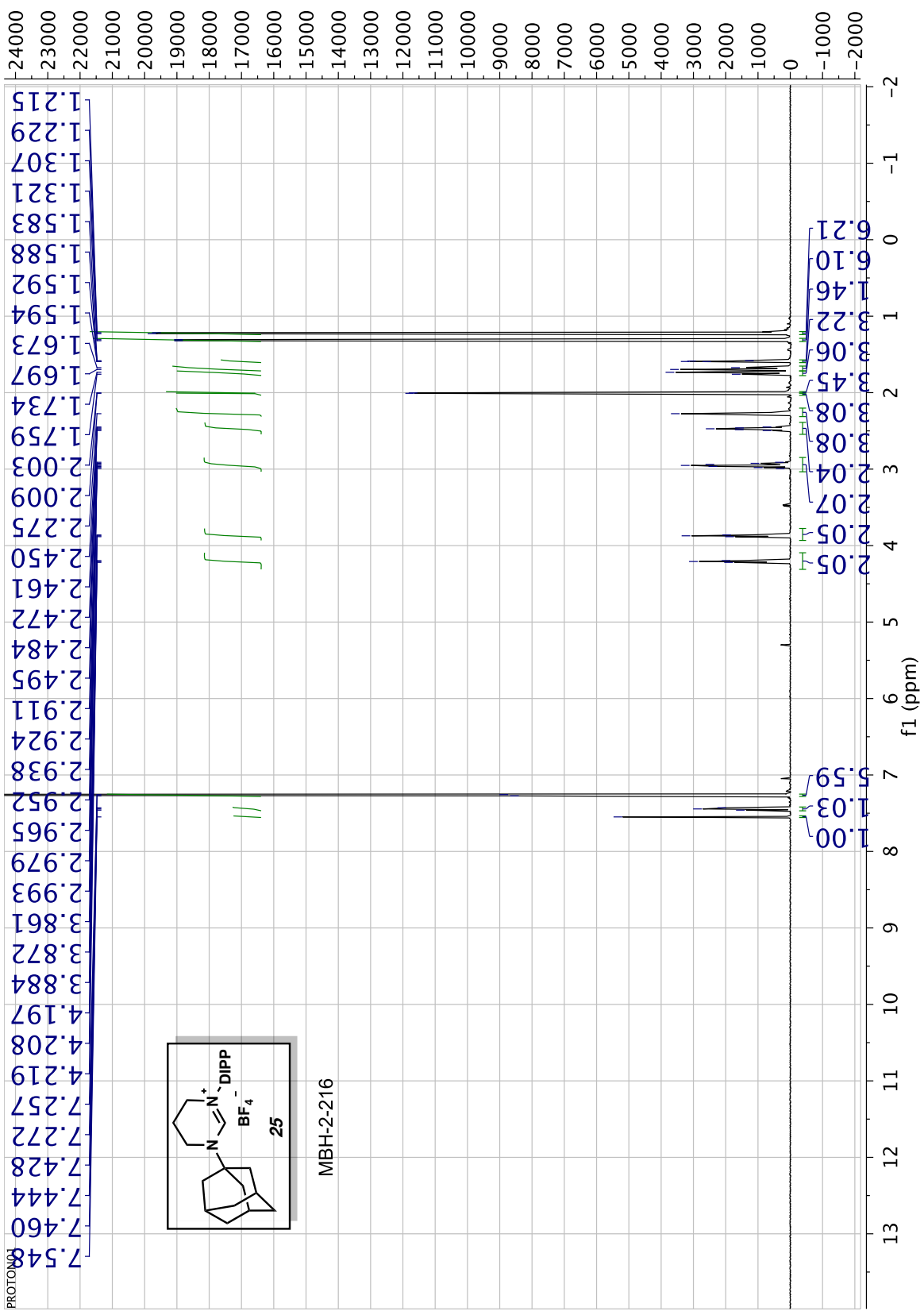

PROTON01
smb-2-90
SI-36
DIPP
Ru
Cl
i-Pr
f1 (ppm)

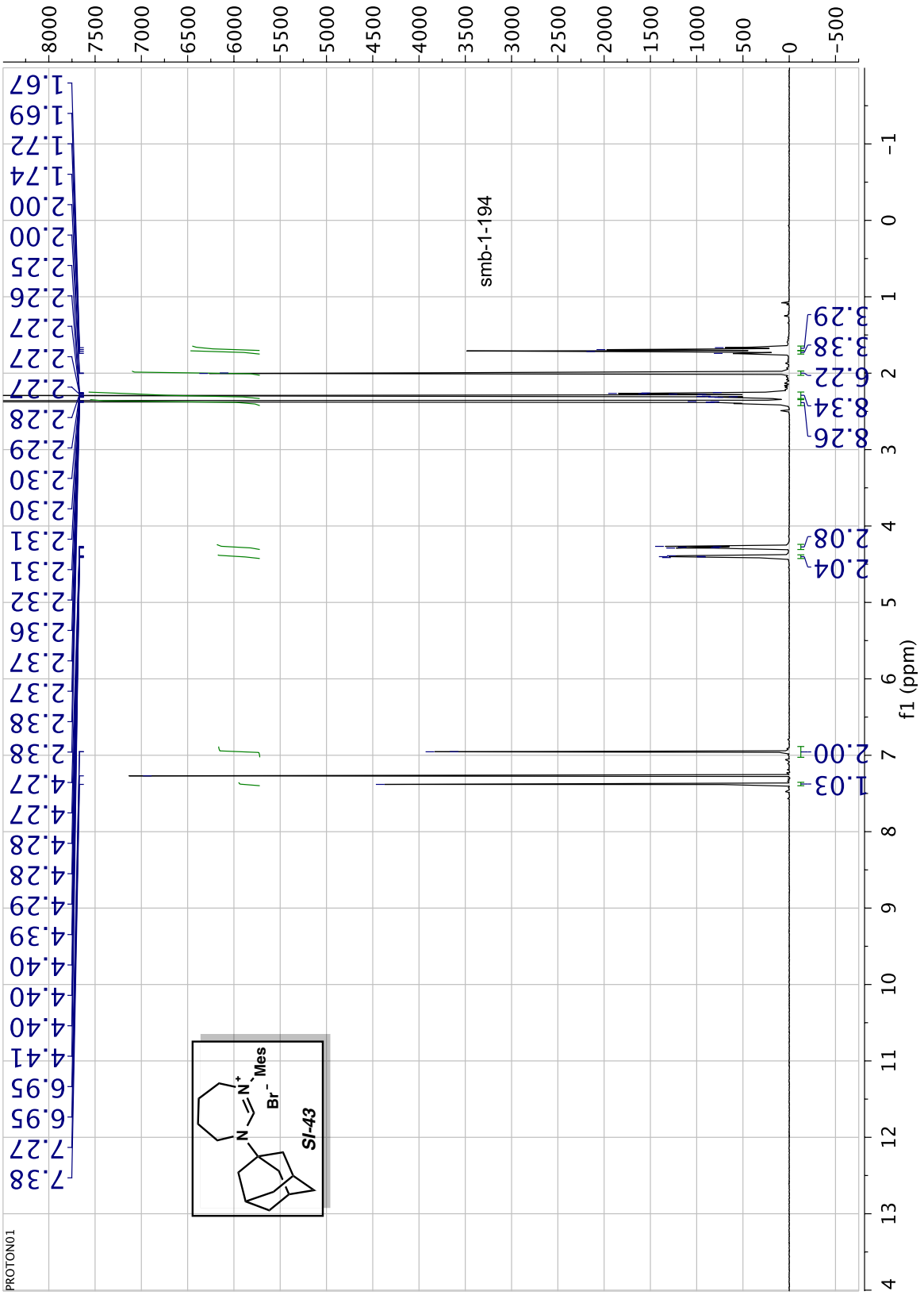

smb-2-236
PROTON01
f1 (ppm)
21
DIPP
i-Pr

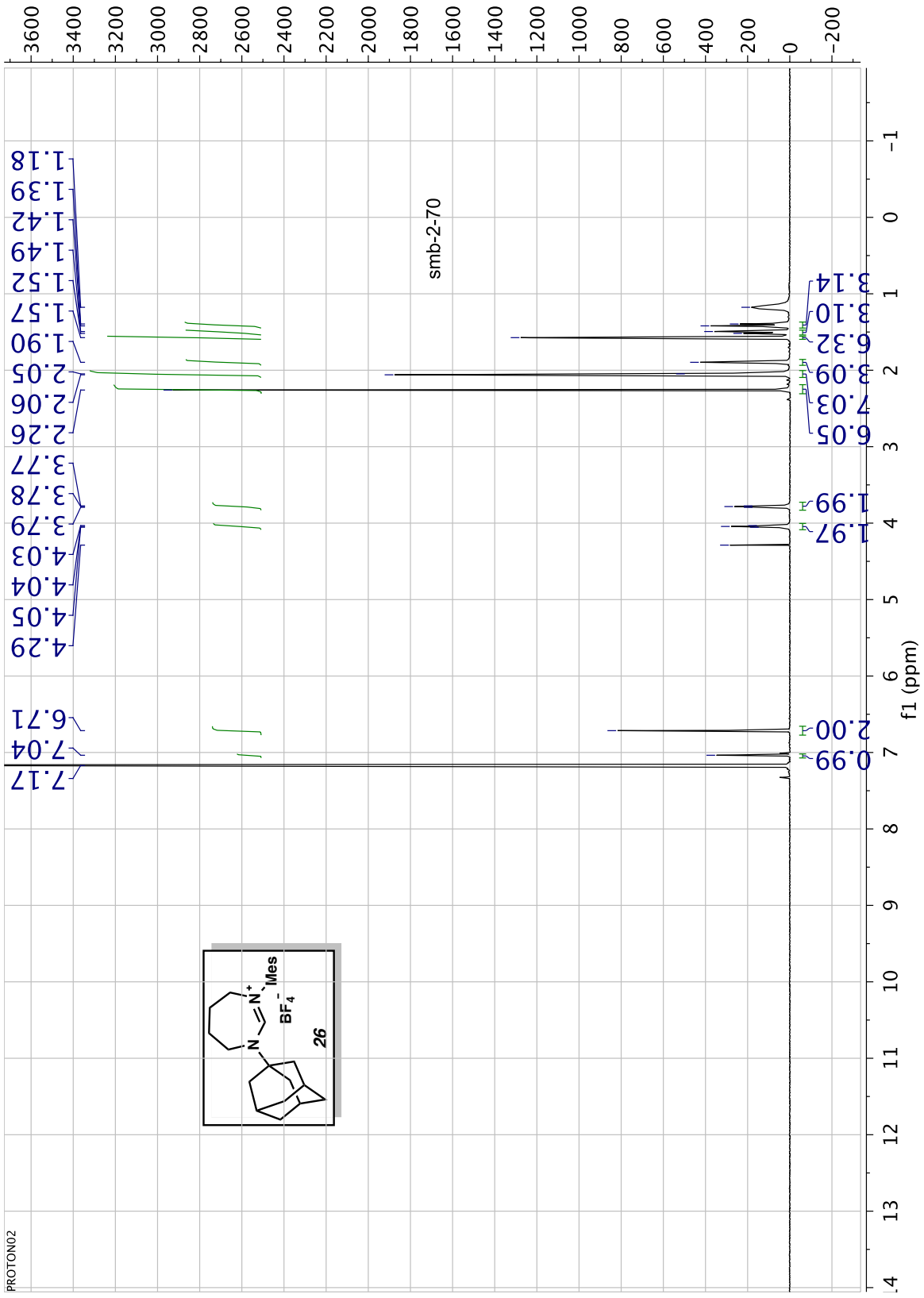

vm-i-43
PROTON02
f1 (ppm)
22
DEP
i-Pr
Ru

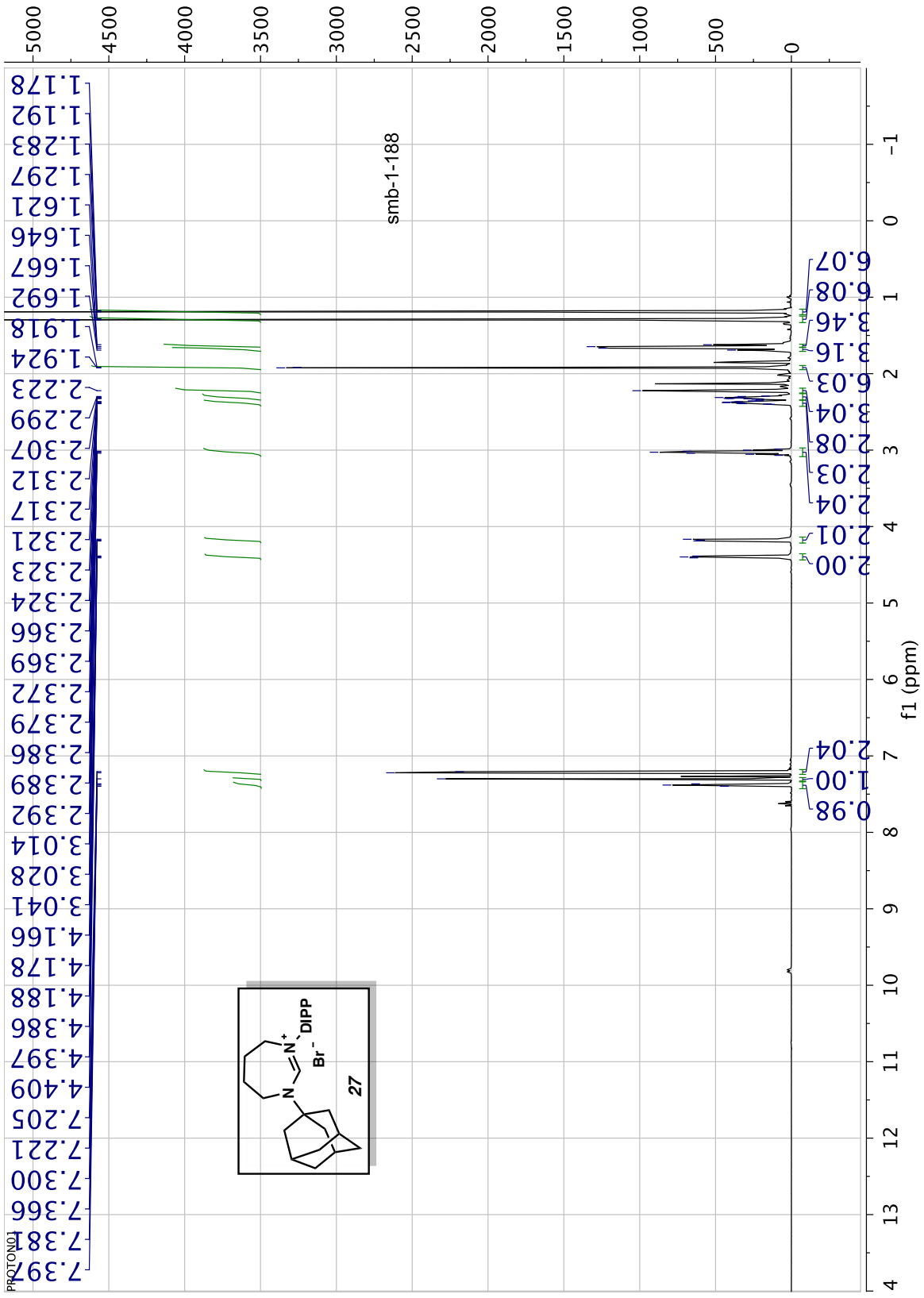

PROTON01
MBH-2-115
f1 (ppm)
8.755
6.950
3.802
2.404
2.316
2.294
2.161
2.155
1.765
1.739
1.721
1.695
3.07
3.20
2.85
3.11
12.03
3.16
3.05
1.97
1.00
Mes
BF4-
23


MBH-2-220
PROTON01
f1 (ppm)
24
DIPP
BF4
1.24
1.25
1.27
1.29
1.56
1.69
1.71
1.74
1.76
2.15
2.16
2.30
2.42
3.05
3.06
3.07
3.09
3.10
3.31
3.88
7.23
7.24
7.42
7.44
7.46
8.88
5.95
5.97
3.29
3.08
2.97
3.06
3.01
3.03
2.00
3.00
0.96
2.02
1.00

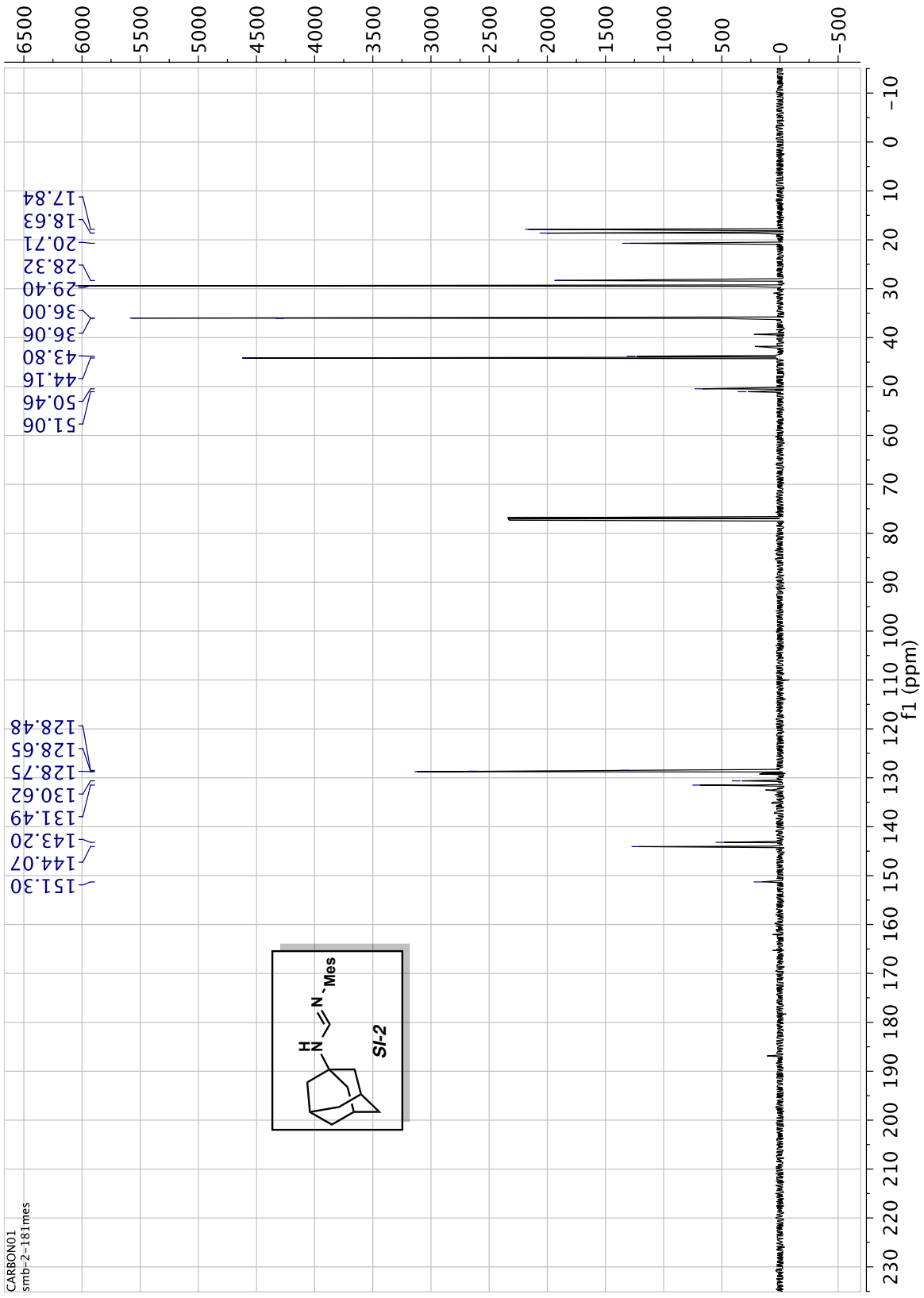

MBH-2-216
25
DIPP
BF4
f1 (ppm)
PROTON01

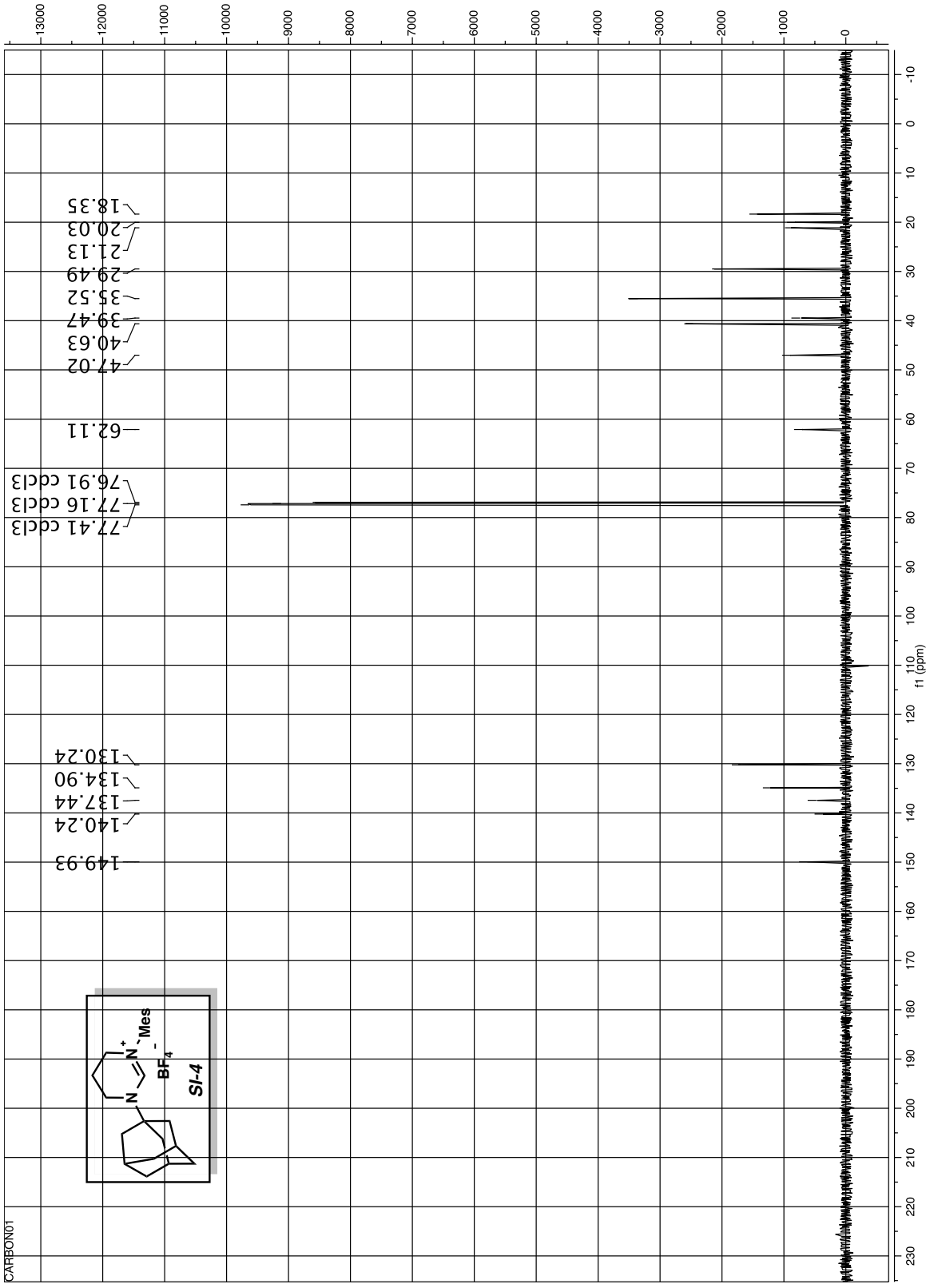

smb-1-194
SI-43
Br⁻
Mes
f1 (ppm)
PROTON01

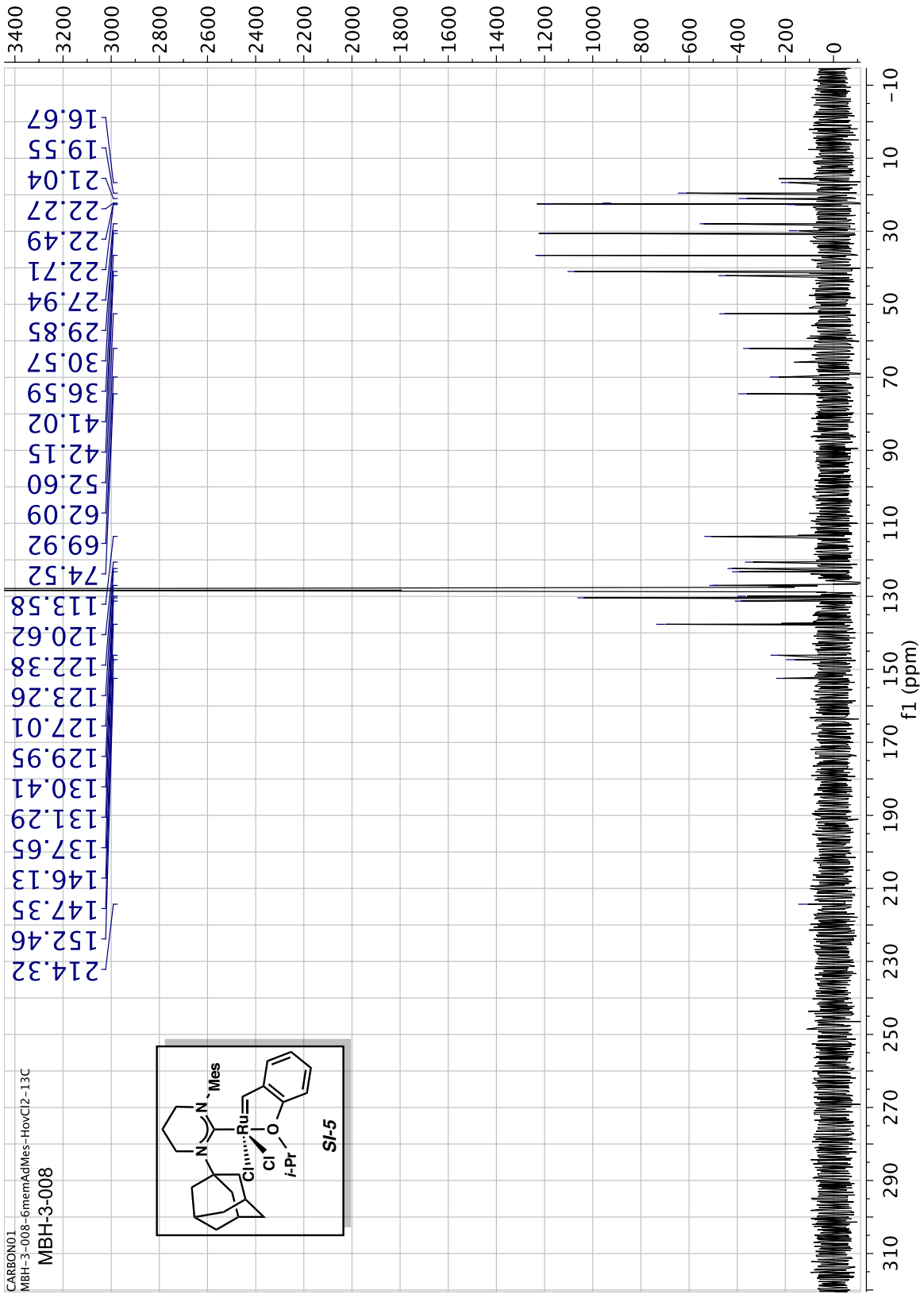

smb-2-70
PROTON02
f1 (ppm)
7.17
7.04
6.71
4.29
4.05
4.04
4.03
3.79
3.78
3.77
2.26
2.06
2.05
1.90
1.57
1.52
1.49
1.42
1.39
1.18
0.99
2.00
1.97
1.99
6.05
7.03
3.09
6.32
3.10
3.14
Mes
BF4
26

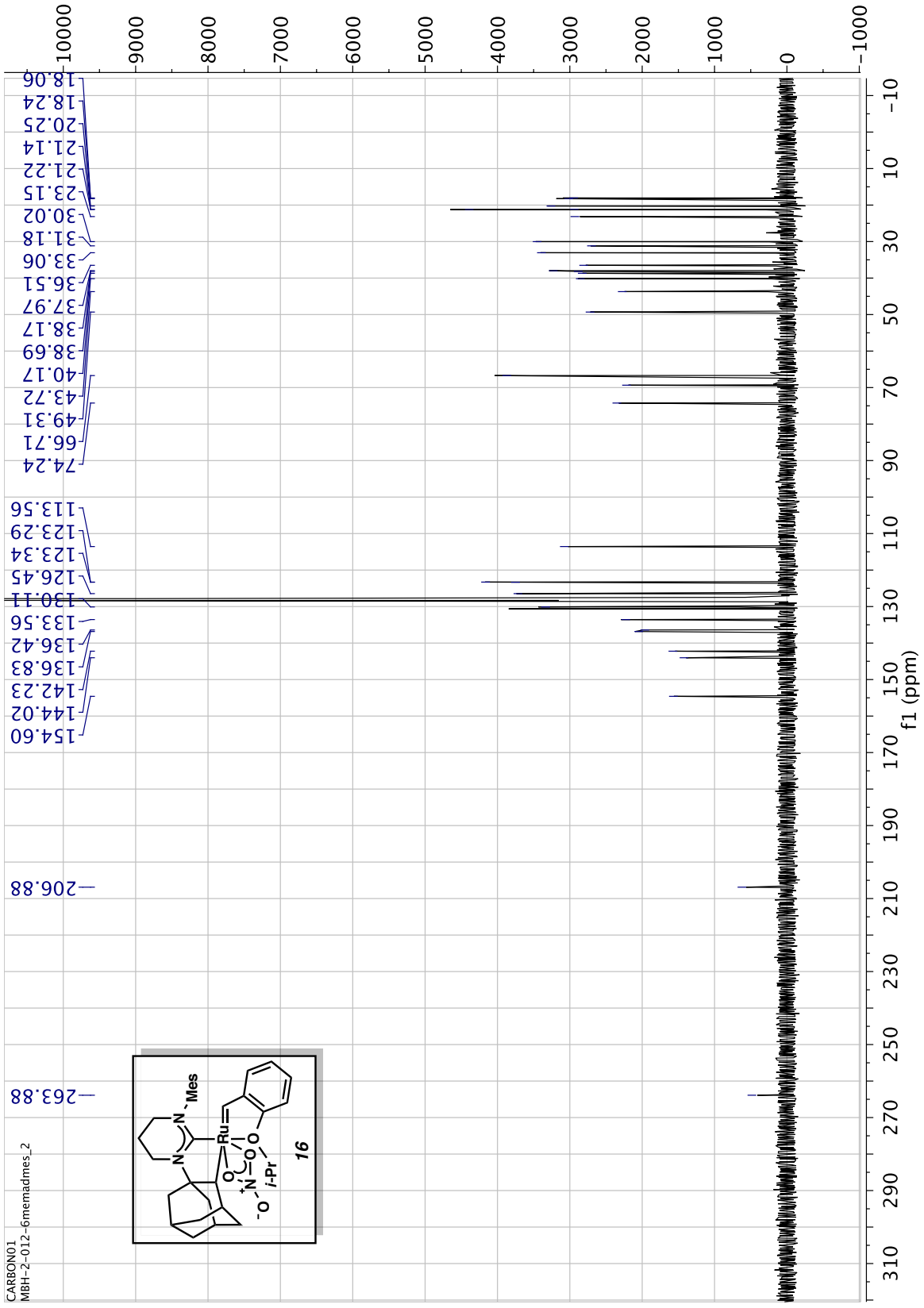

smb-1-188
PROTON01
f1 (ppm)
DIPP
Br⁻
27

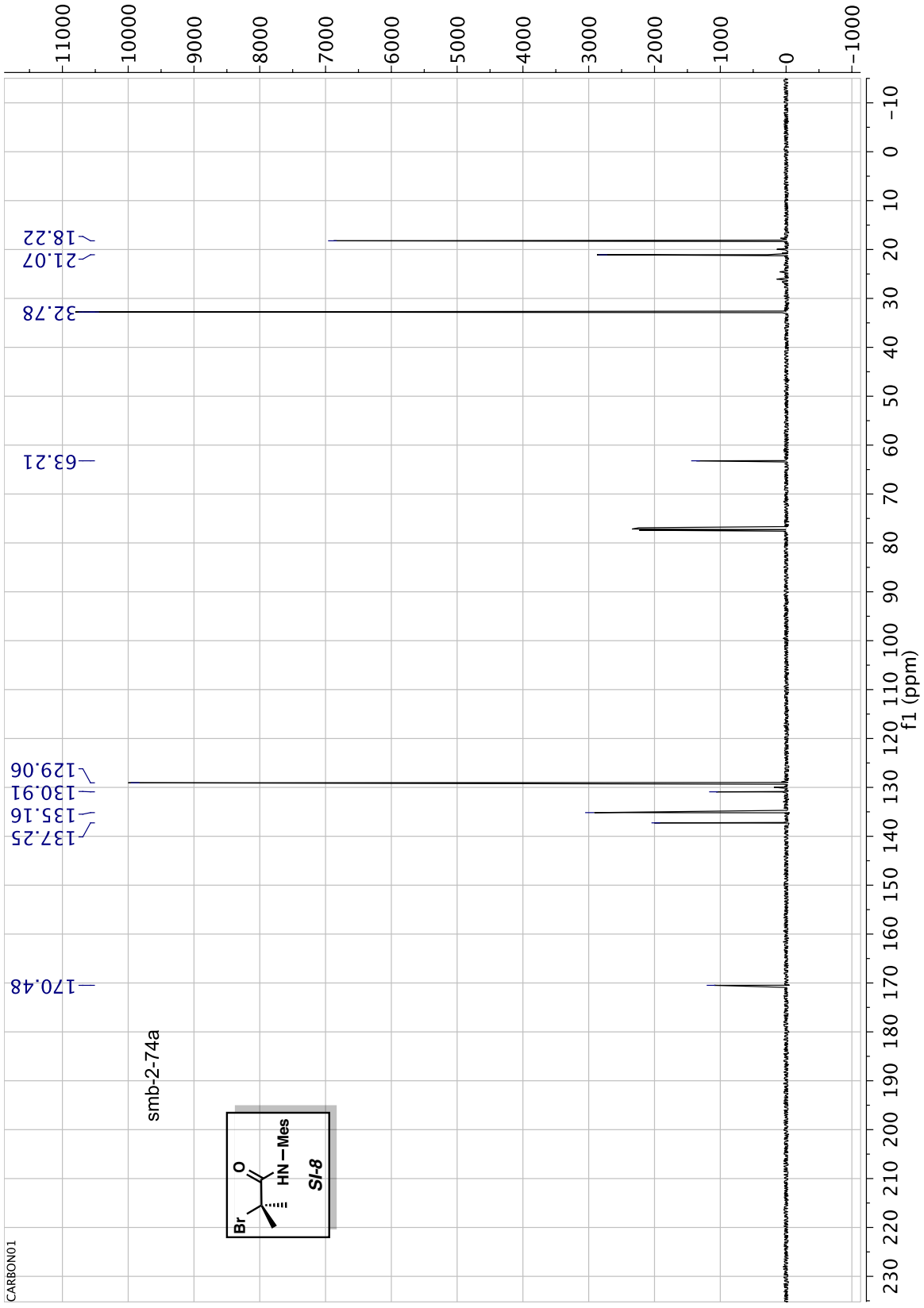
^{13}C NMR Spectra:

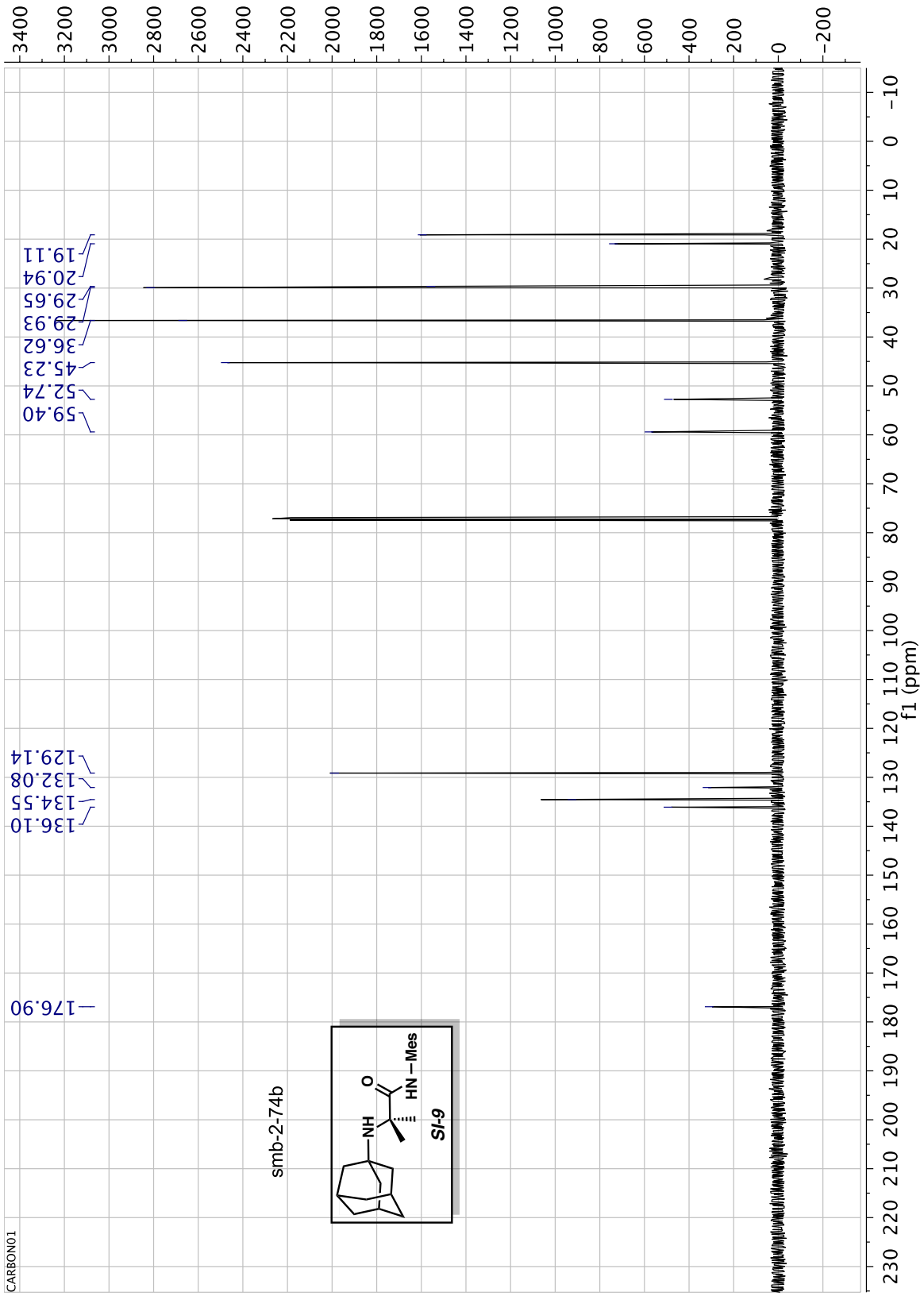

CARBON01
smb-2-181mes
17.84
18.63
20.71
28.32
29.40
36.00
36.06
43.80
44.16
50.46
51.06
128.48
128.65
128.75
130.62
131.49
143.20
144.07
151.30
Mes
SI-2
f1 (ppm)

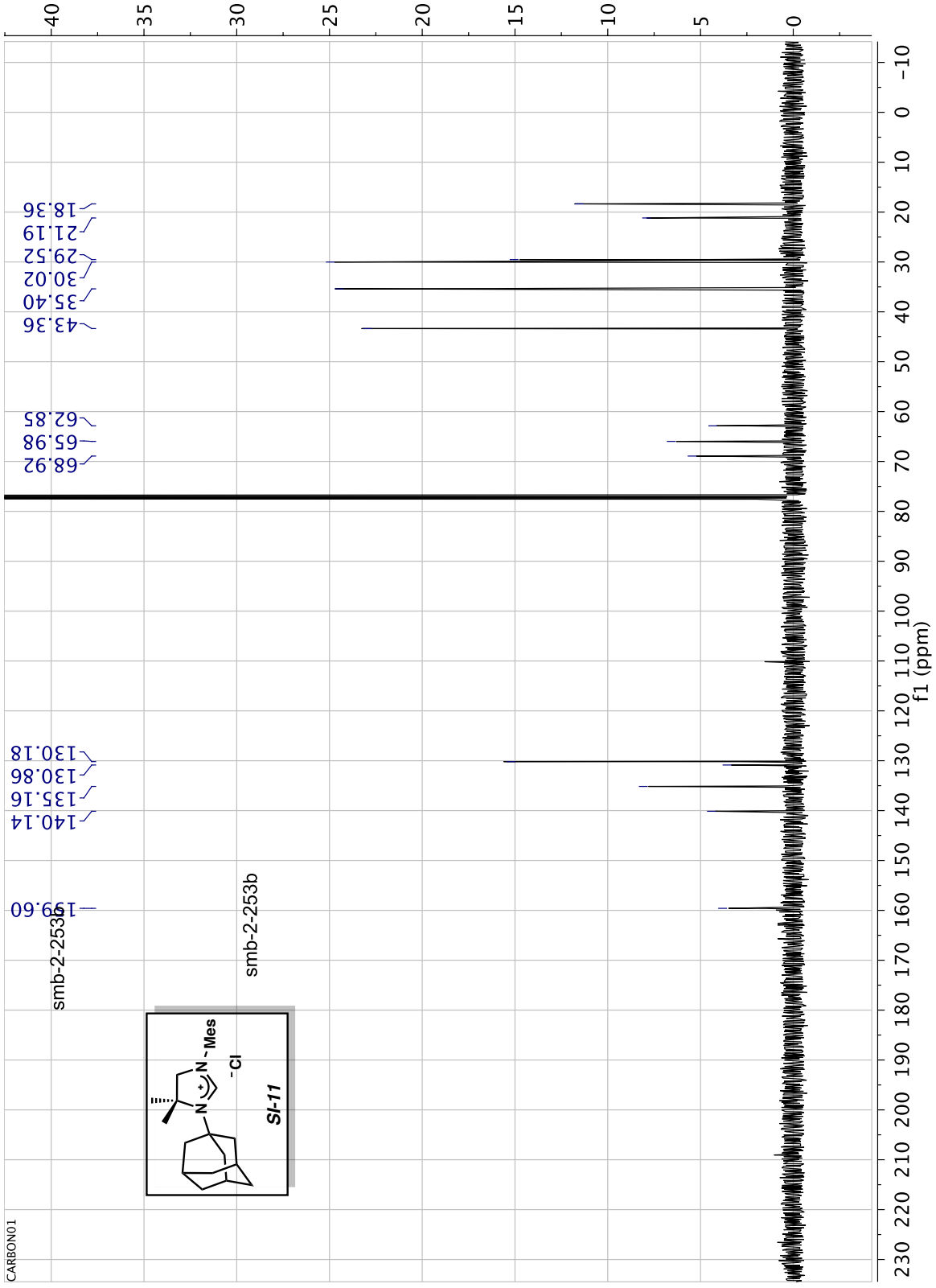

CARBON01
SI-4
Mes
BF4
18.35
20.03
21.13
29.49
35.52
39.47
40.63
47.02
62.11
76.91 cdcl3
77.16 cdcl3
77.41 cdcl3
130.24
134.90
137.44
140.24
149.93
f1 (ppm)

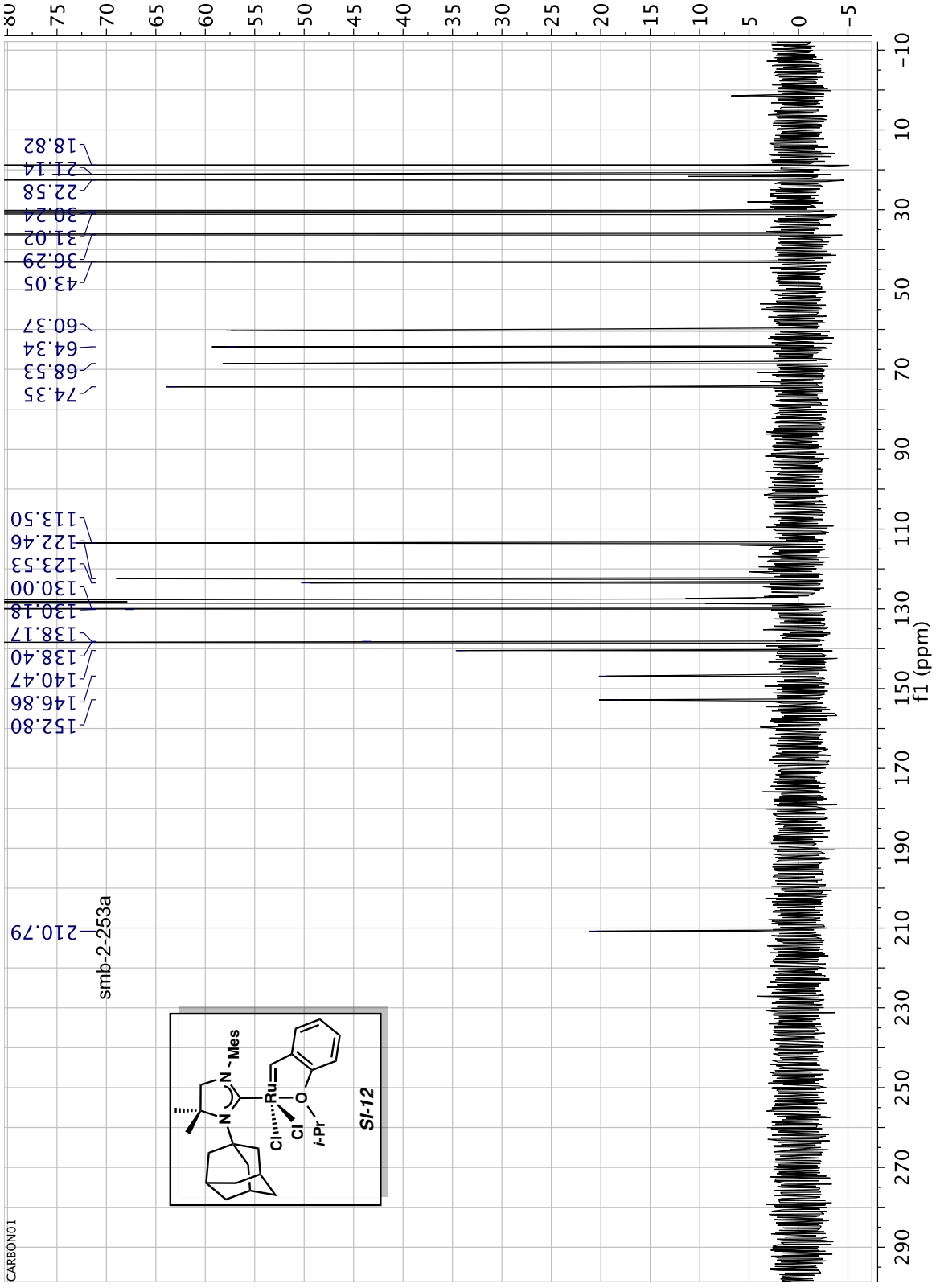

CARBON01
MBH-3-008-6memAdMes-HovCl2-13C
MBH-3-008
SI-5
f1 (ppm)
214.32
152.46
147.35
146.13
137.65
131.29
130.41
129.95
127.01
123.26
122.38
120.62
113.58
74.52
69.92
62.09
52.60
42.15
41.02
36.59
30.57
29.85
27.94
22.71
22.49
22.27
21.04
19.55
16.67

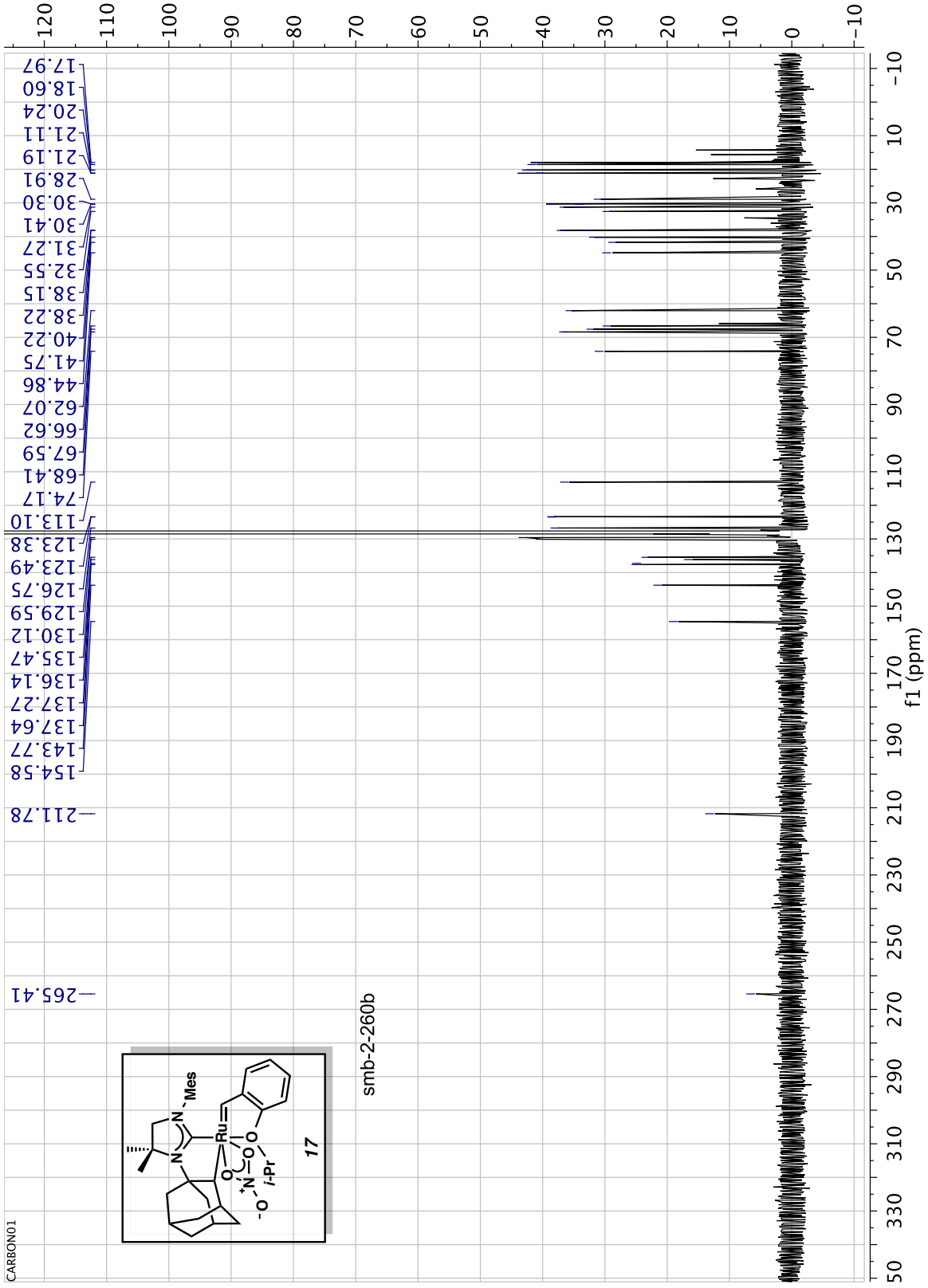

CARBON01
MBH-2-012-6memadmes_2
f1 (ppm)
16
Mes
i-Pr
Ru


CARBON01
smb-2-74a
Br
O
HN—Mes
SI-8
170.48
137.25
135.16
130.91
129.06
63.21
32.78
21.07
18.22
f1 (ppm)


CARBON01
smb-2-74b
SI-9
NH
HN
Mes
O
176.90
136.10
134.55
132.08
129.14
59.40
52.74
45.23
36.62
29.93
29.65
20.94
19.11
f1 (ppm)


CARBON01
smb-2-253b
smb-2-253b
SI-11
Mes
Cl
f1 (ppm)
199.60
140.14
135.16
130.86
130.18
68.92
65.98
62.85
43.36
35.40
30.02
29.52
21.19
18.36


CARBON01
smb-2-253a
210.79
152.80
146.86
140.47
138.40
138.17
130.18
130.00
123.53
122.46
113.50
74.35
68.53
64.34
60.37
43.05
36.29
31.02
30.24
22.58
21.14
18.82
N
Mes
N
Ru
Cl
Cl
O
i-Pr
SI-12
f1 (ppm)


CARBON01
smb-2-260b
17
Mes
i-Pr
Ru
f1 (ppm)
265.41
211.78
154.58
143.77
137.64
137.27
136.14
135.47
130.12
129.59
126.75
123.49
123.38
113.10
74.17
68.41
67.59
66.62
62.07
44.86
41.75
40.22
38.22
38.15
32.55
31.27
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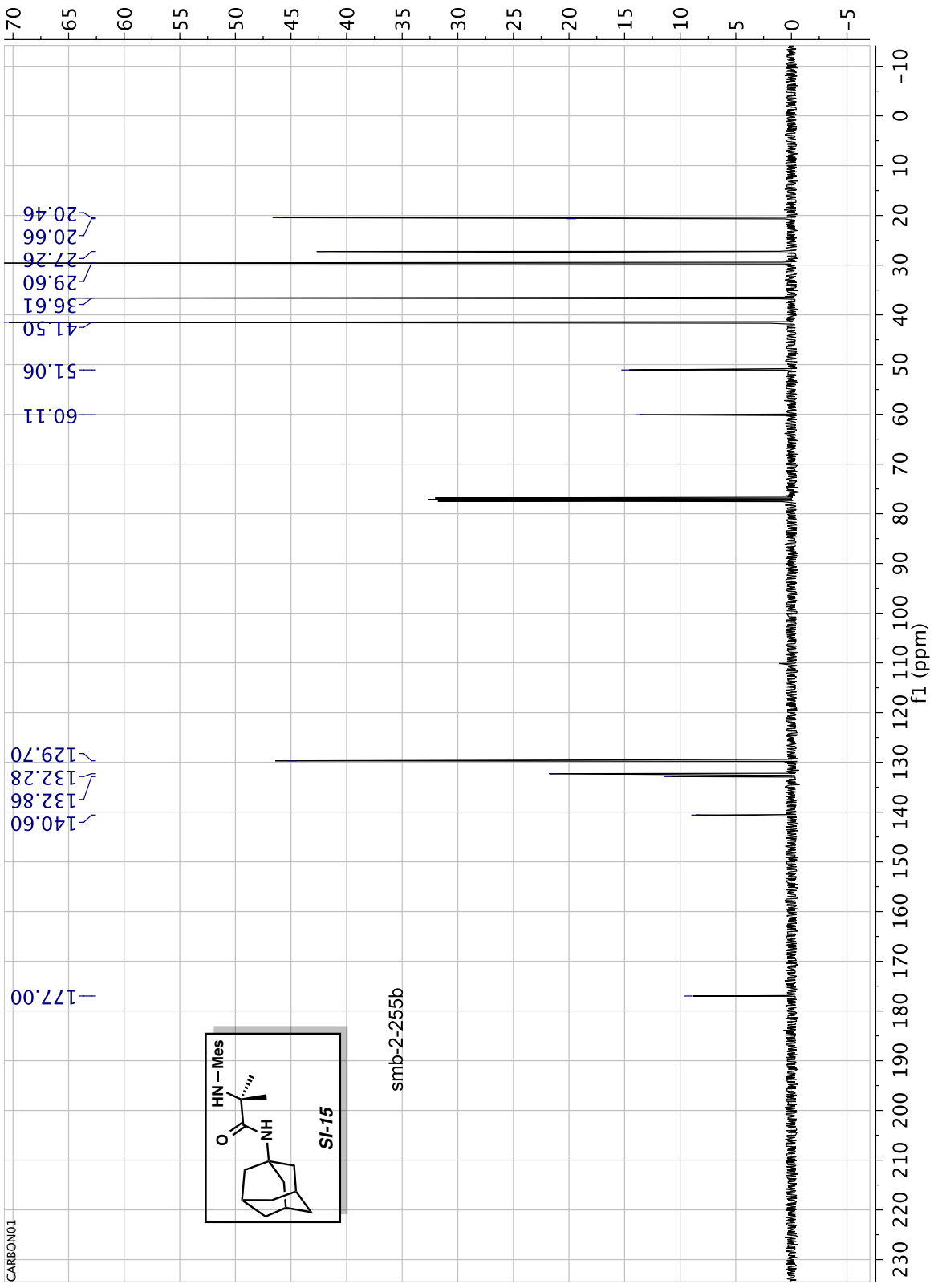
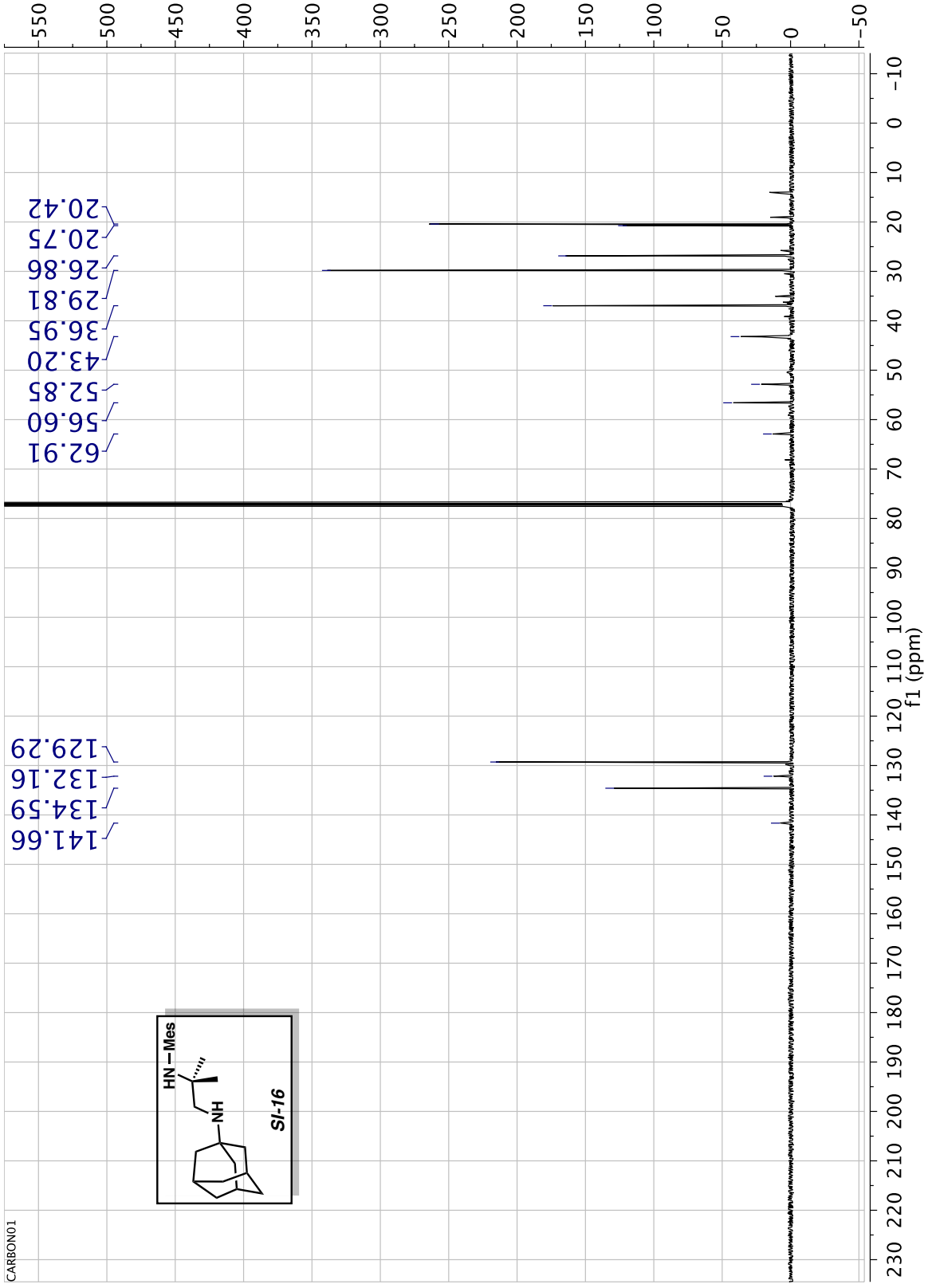
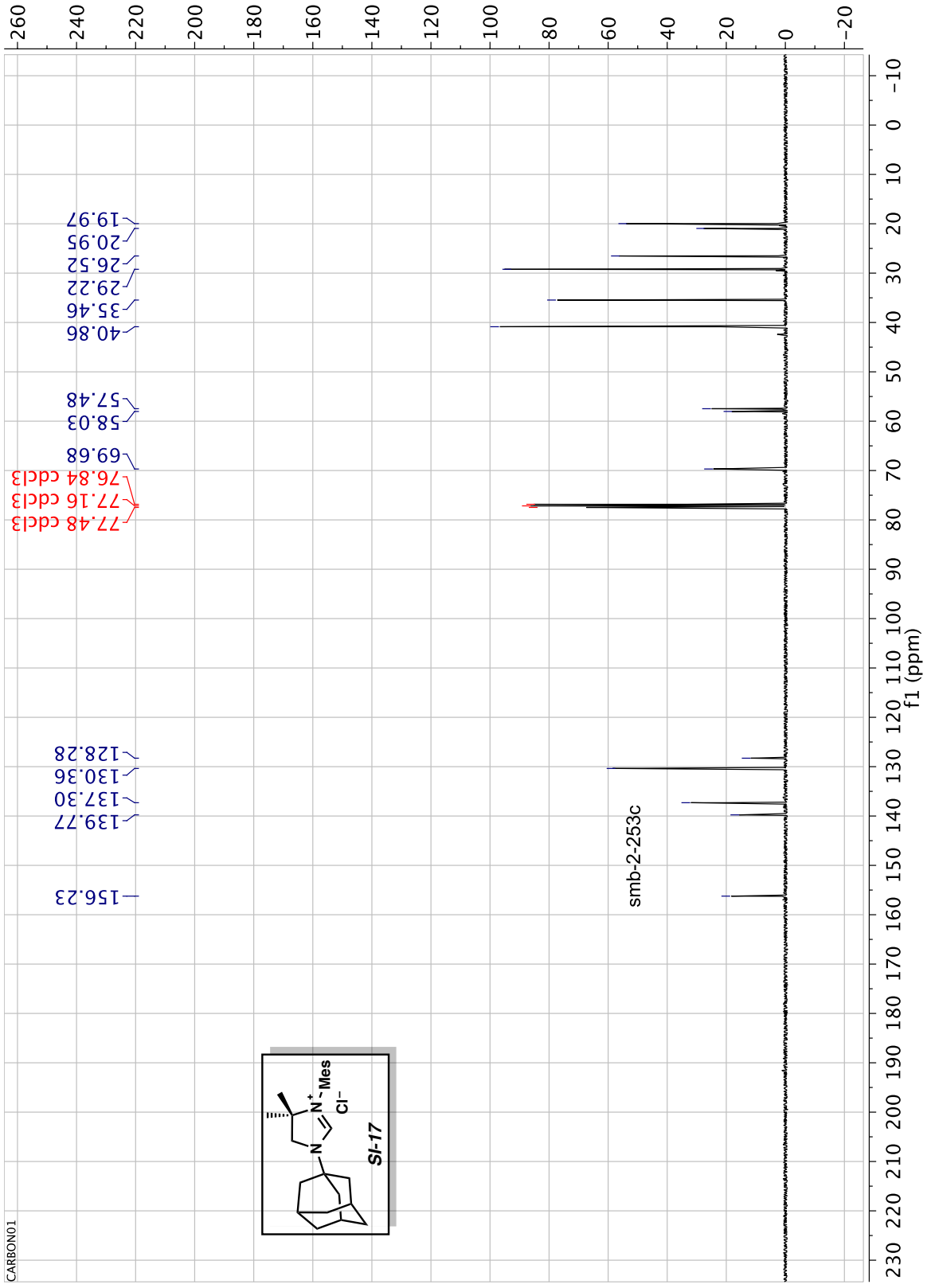
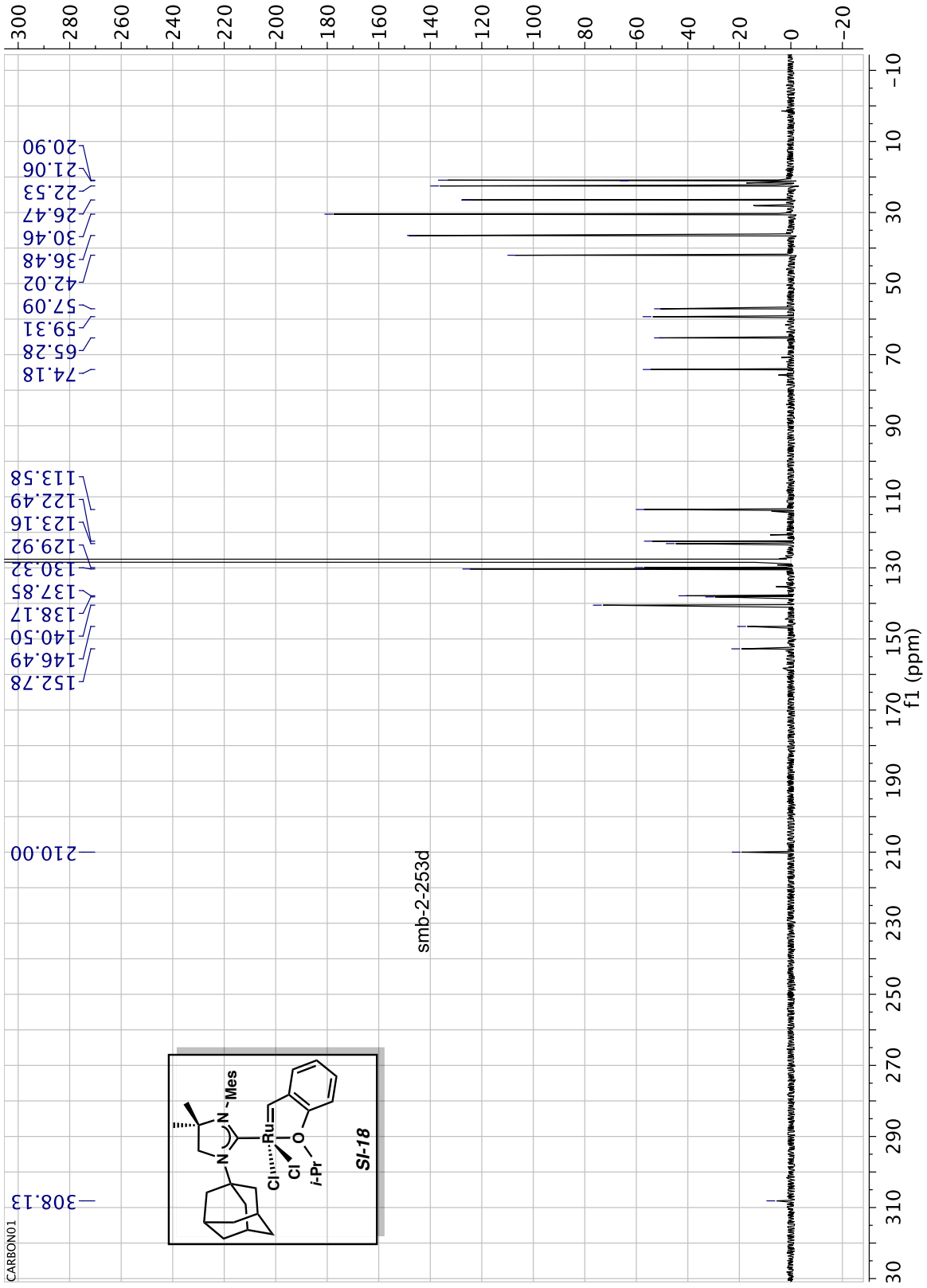
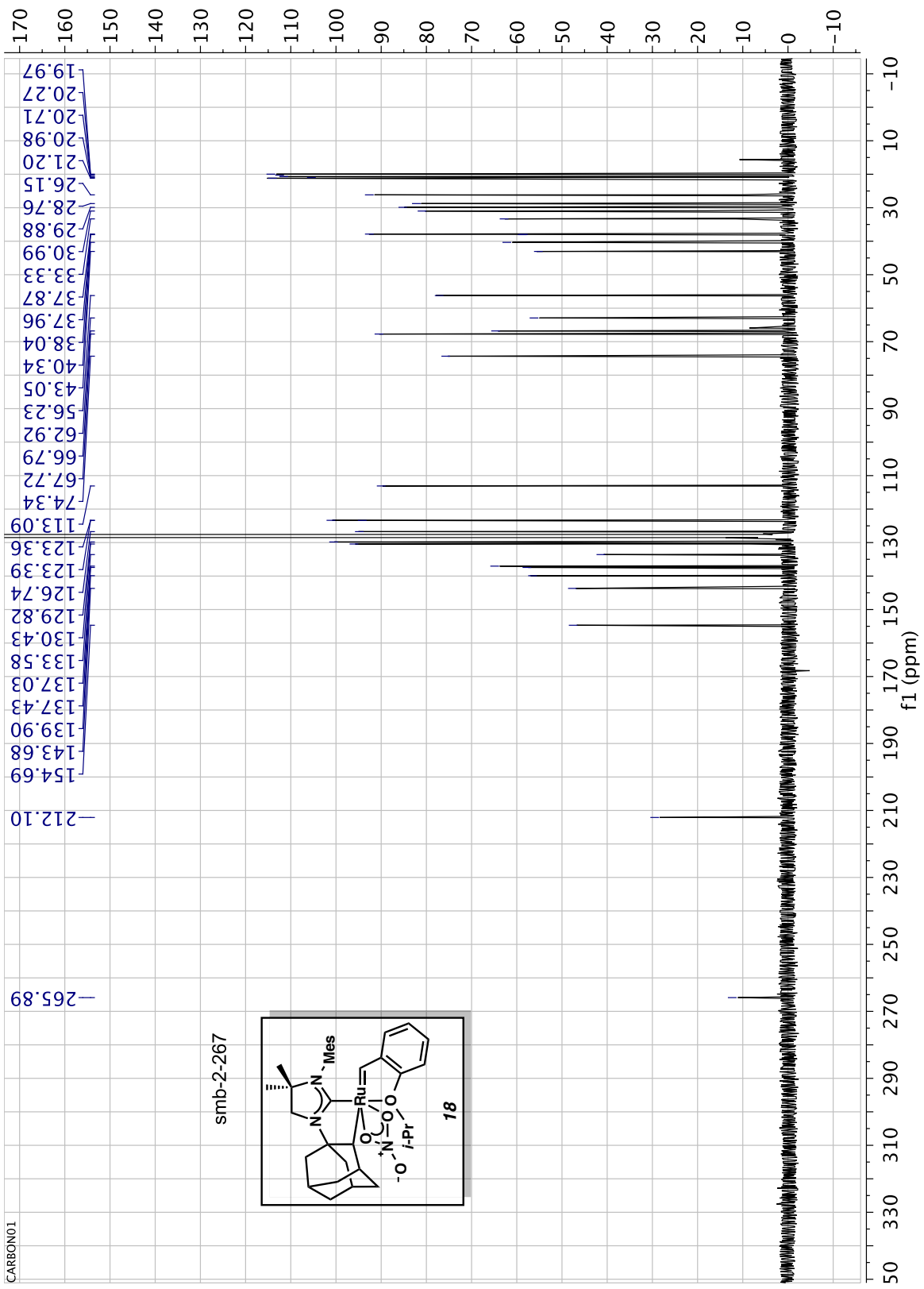
30.30
28.91
21.19
21.11
20.24
18.60
17.97

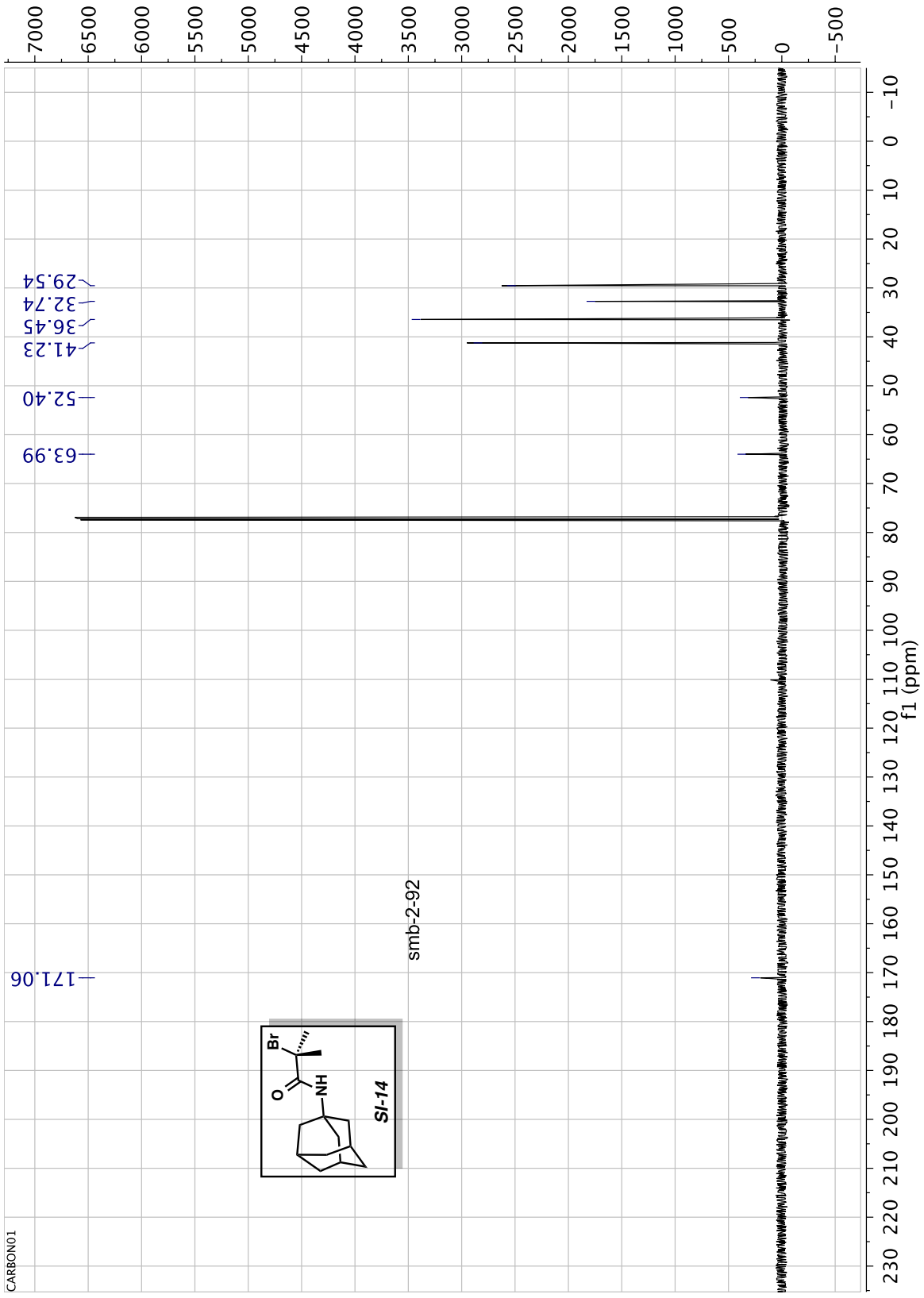

CARBON01
smb-2-255b
SI-15
HN—Mes
O
NH
177.00
140.60
132.86
132.28
129.70
60.11
51.06
41.50
36.61
29.60
27.26
20.66
20.46
f1 (ppm)

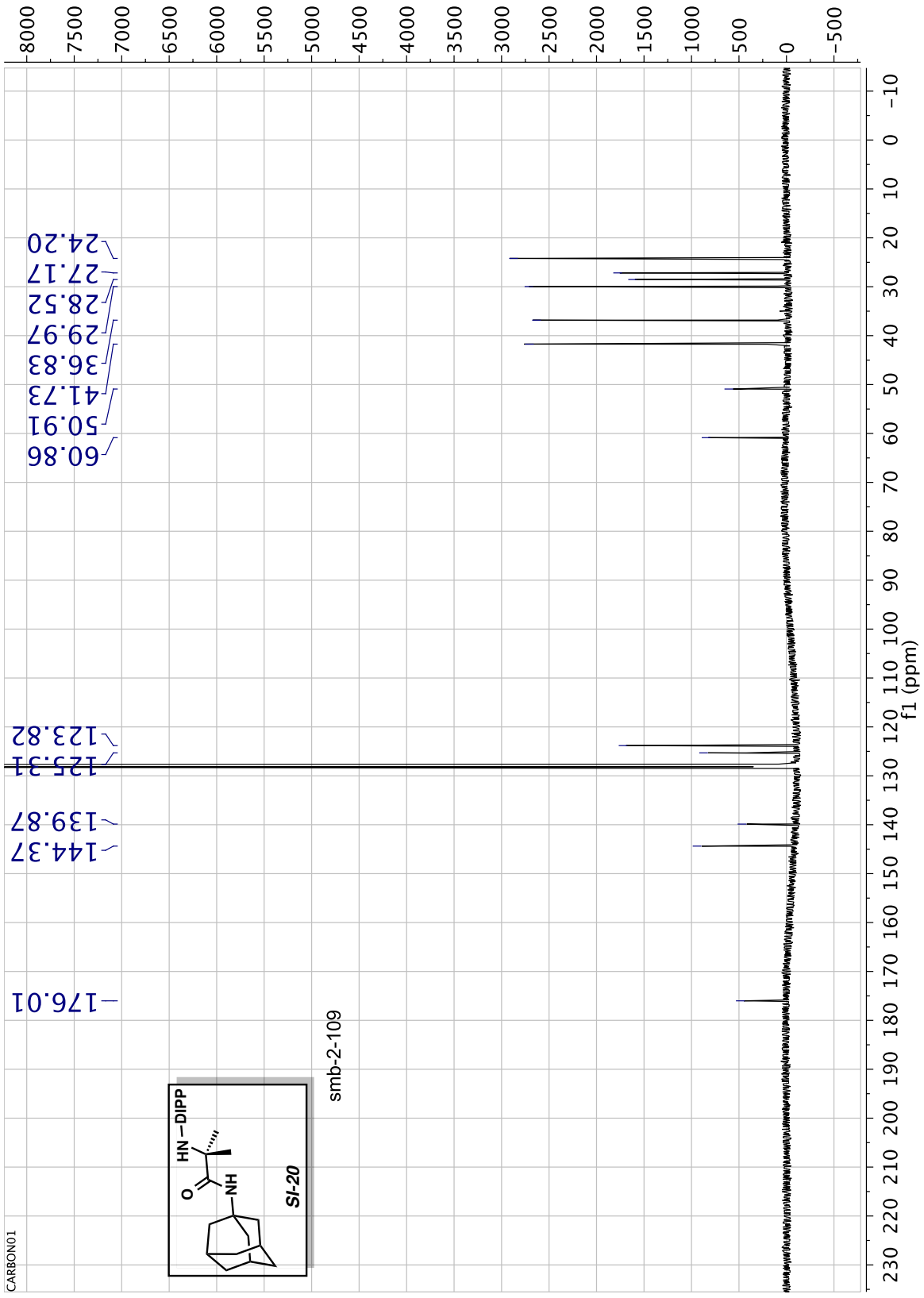

CARBON01
HN—Mes
NH
SI-16
141.66
134.59
132.16
129.29
62.91
56.60
52.85
43.20
36.95
29.81
26.86
20.75
20.42
f1 (ppm)

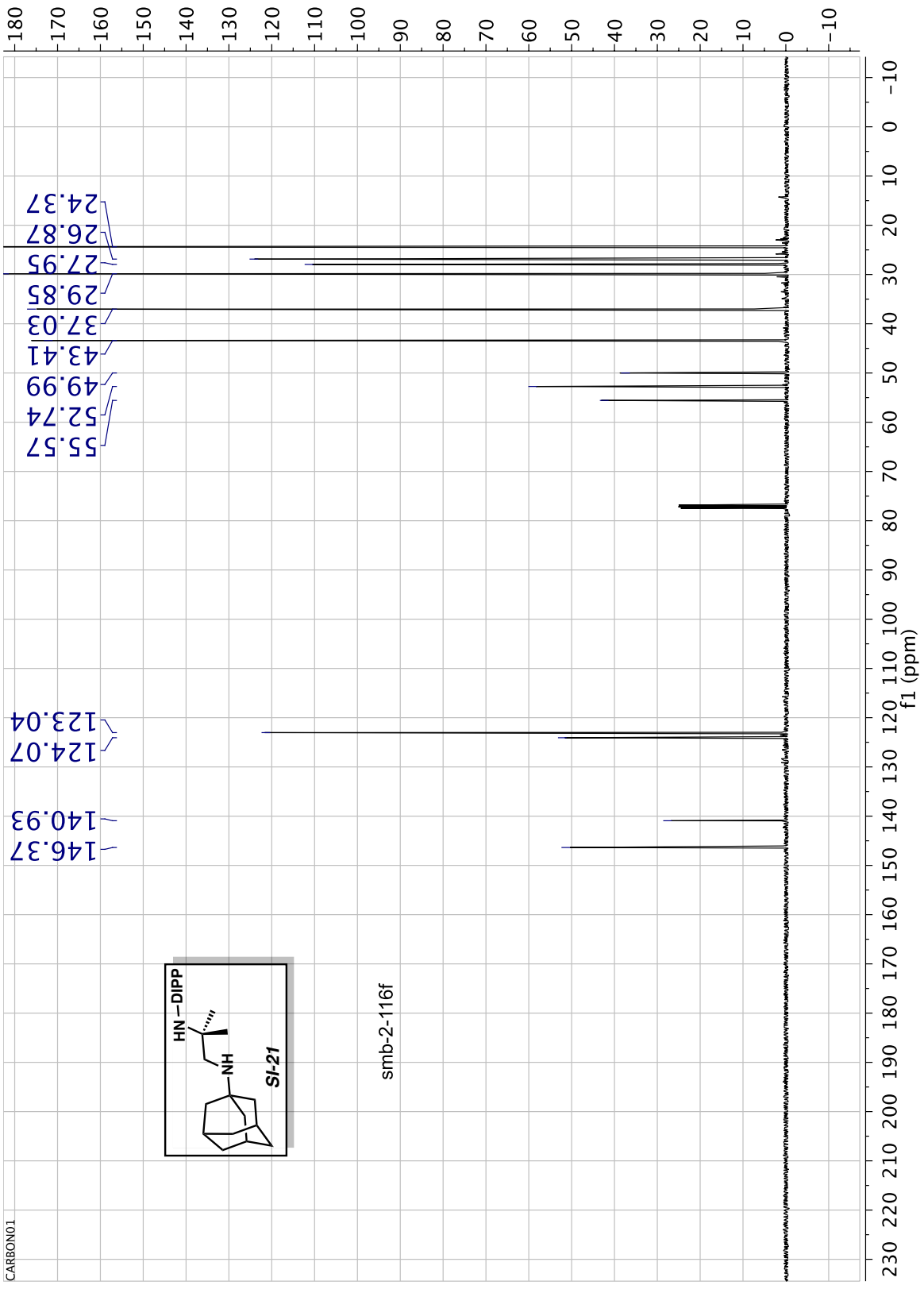

CARBON01
smb-2-253c
SI-17
Mes
Cl⁻
f1 (ppm)
19.97
20.95
26.52
29.22
35.46
40.86
57.48
58.03
69.68
76.84 cdcl3
77.16 cdcl3
77.48 cdcl3
128.28
130.36
137.30
139.77
156.23

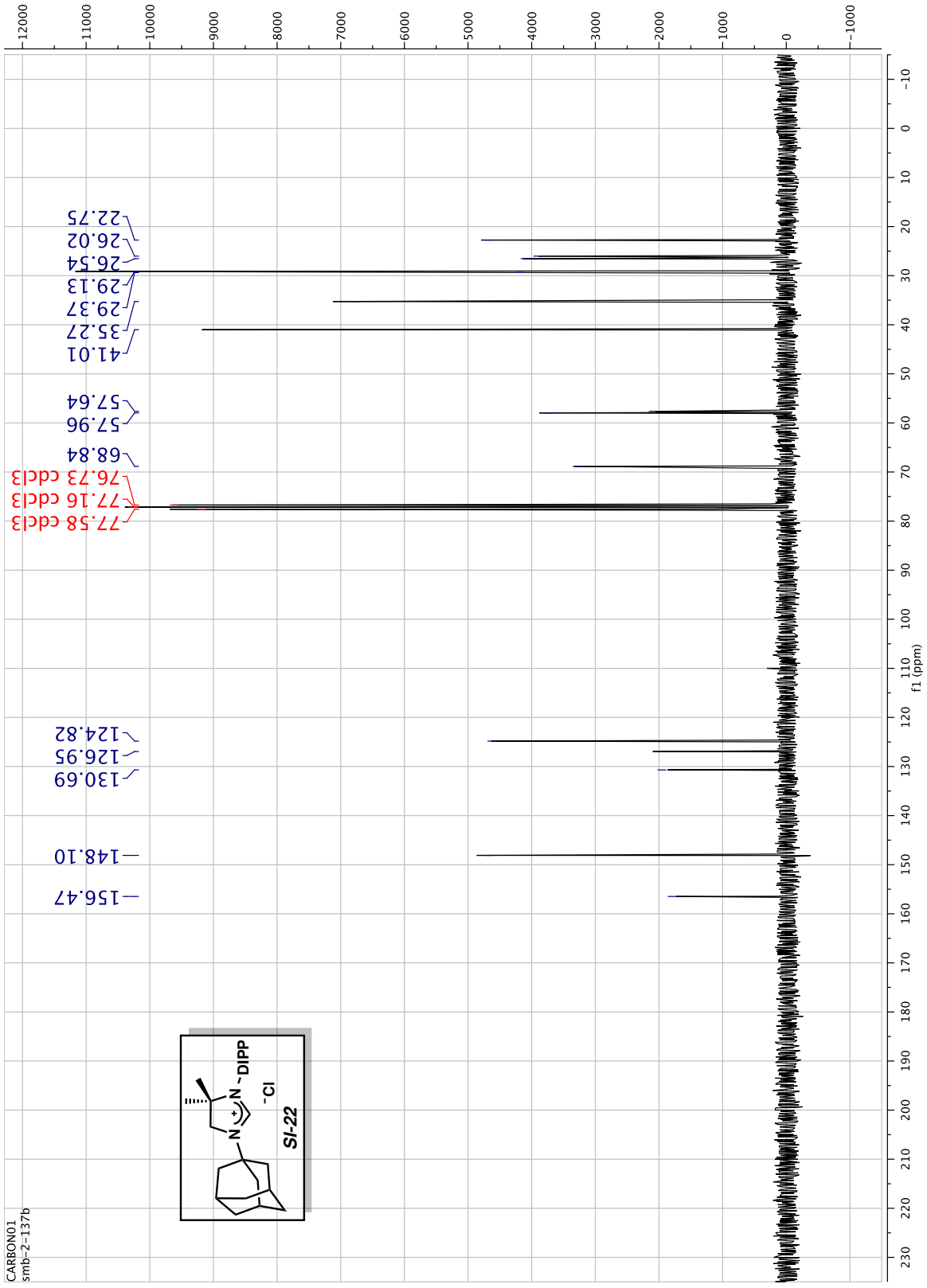

CARBON01
smb-2-253d
SI-18
f1 (ppm)
308.13
210.00
152.78
146.49
140.50
138.17
137.85
130.32
129.92
123.16
122.49
113.58
74.18
65.28
59.31
57.09
42.02
36.48
30.46
26.47
22.53
21.06
20.90

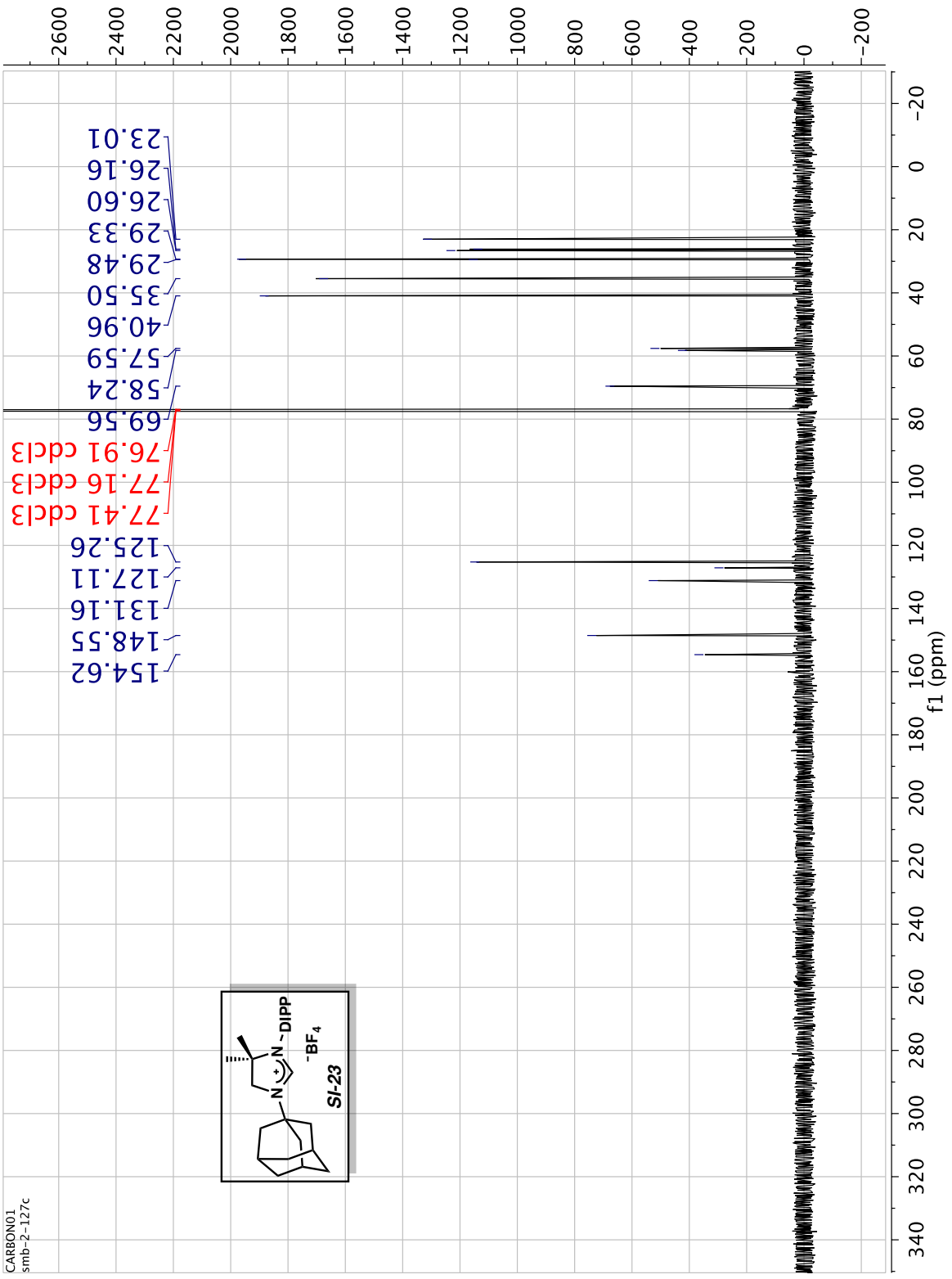

CARBON01
smb-2-267
Mes
Ru
i-Pr
18
f1 (ppm)
19.97
20.27
20.71
20.98
21.20
26.15
28.76
29.88
30.99
33.33
37.87
37.96
38.04
40.34
43.05
56.23
62.92
66.79
67.72
74.34
113.09
123.36
123.39
126.74
129.82
130.43
133.58
137.03
137.43
139.90
143.68
154.69
212.10
265.89

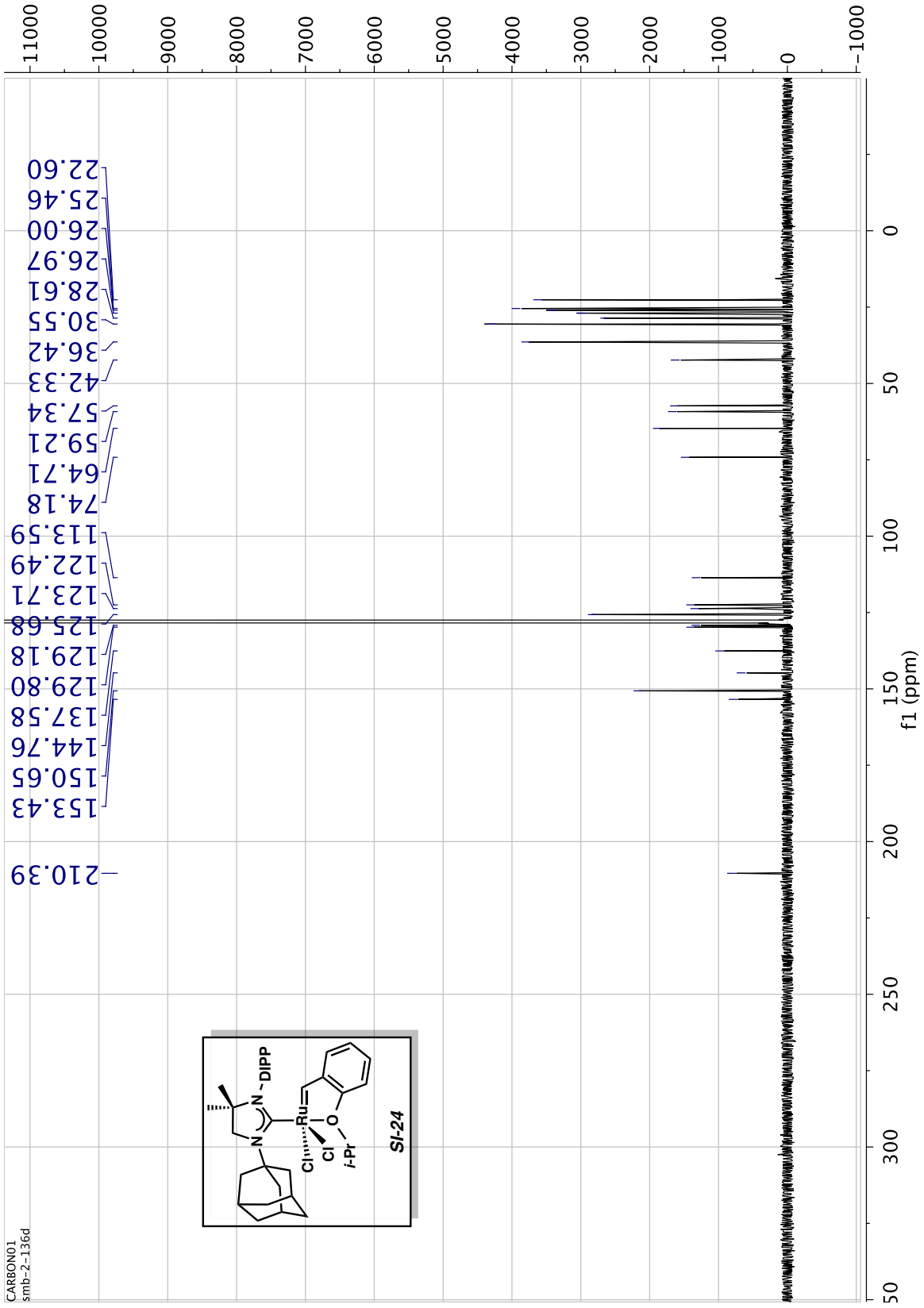

CARBON01
smb-2-92
SI-14
Br
O
NH
171.06
63.99
52.40
41.23
36.45
32.74
29.54
f1 (ppm)

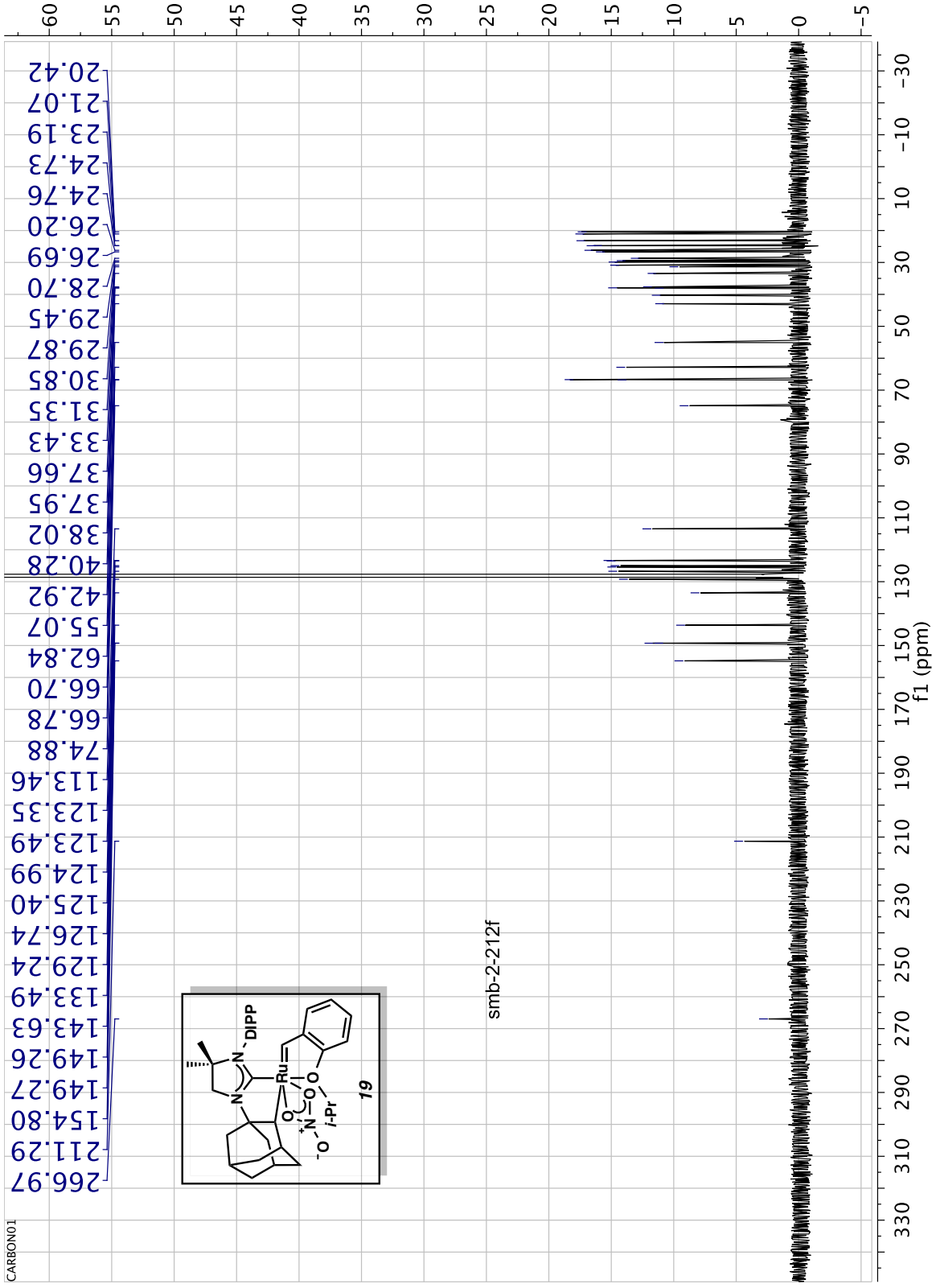

CARBON01
smb-2-109
HN—DIPP
NH
O
SI-20
176.01
144.37
139.87
125.31
123.82
60.86
50.91
41.73
36.83
29.97
28.52
27.17
24.20
f1 (ppm)

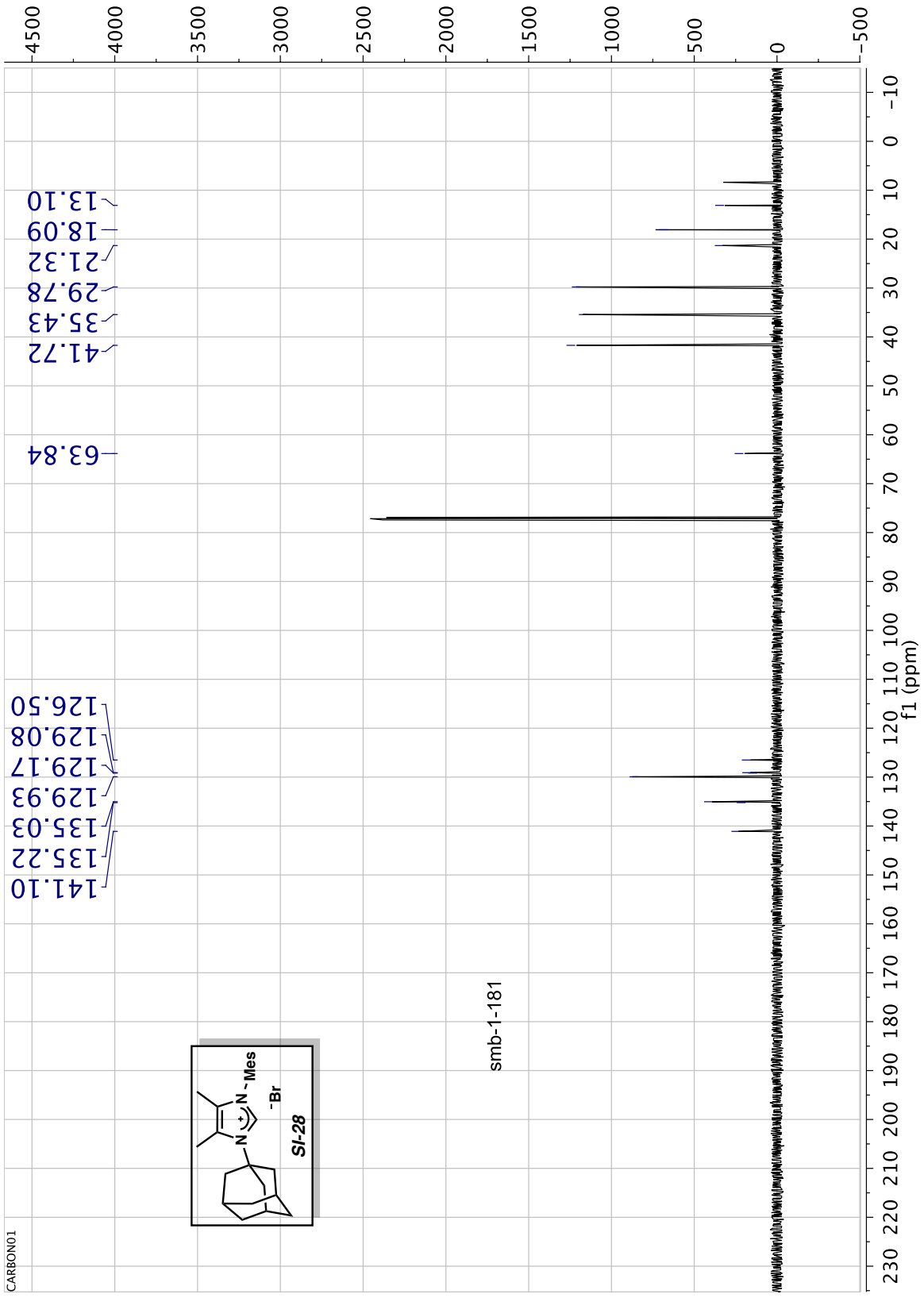

CARBON01
smb-2-116f
HN—DIPP
NH
SI-21
146.37
140.93
124.07
123.04
55.57
52.74
49.99
43.41
37.03
29.85
27.95
26.87
24.37
f1 (ppm)

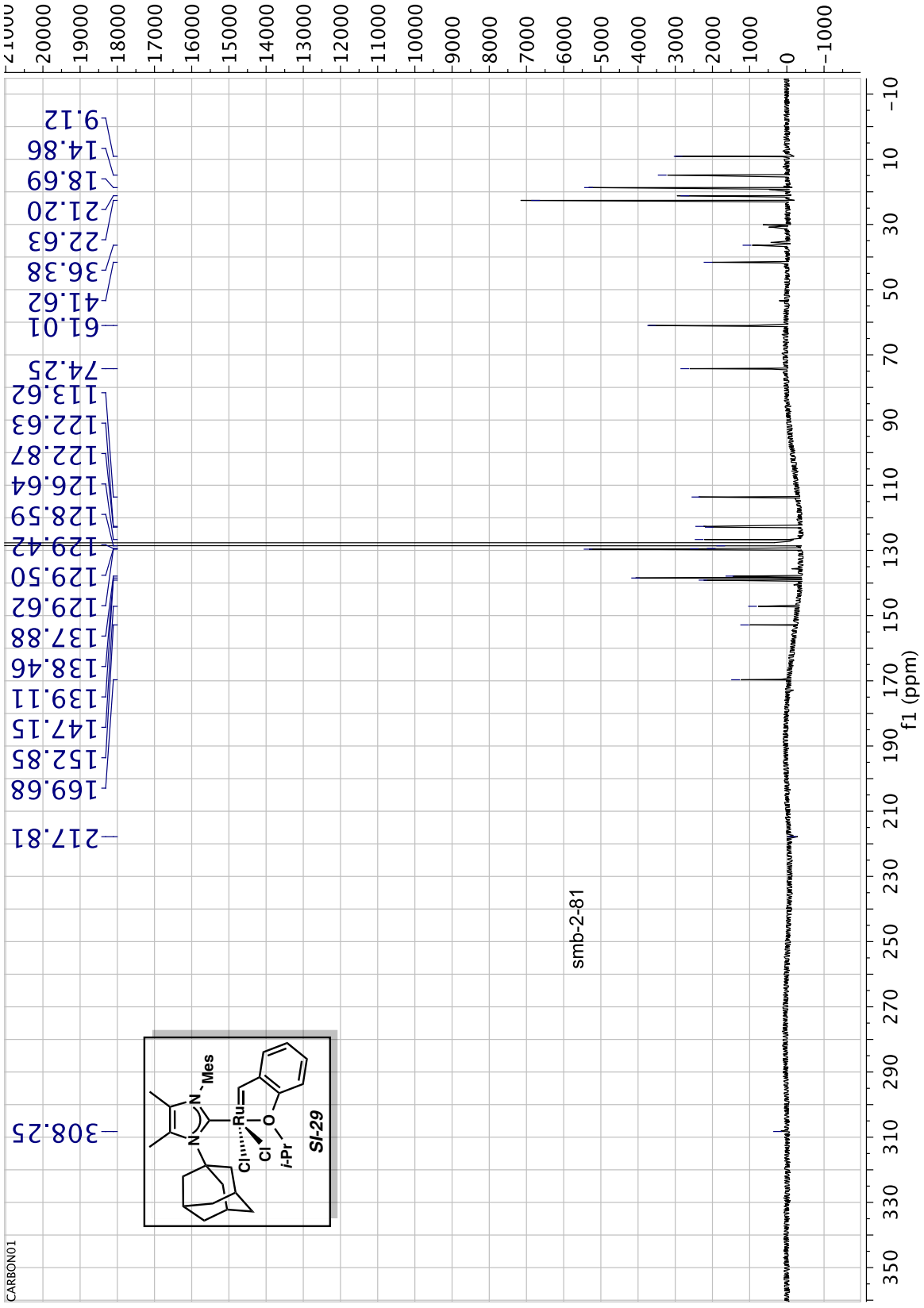

22.75
26.02
26.54
29.13
29.37
35.27
41.01
57.64
57.96
68.84
76.73 cdcl3
77.16 cdcl3
77.58 cdcl3
124.82
126.95
130.69
148.10
156.47
SI-22
DIPP
Cl
CARBON01
smb-2-137b
f1 (ppm)


154.62
148.55
131.16
127.11
125.26
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
69.56
58.24
57.59
40.96
35.50
29.48
29.33
26.60
26.16
23.01
SI-23
N
N
DIPP
BF4
f1 (ppm)
CARBON01
smb-2-127c


CARBON01
smb-2-136d
SI-24
DIPP
Ru
Cl
i-Pr
f1 (ppm)
210.39
153.43
150.65
144.76
137.58
129.80
129.18
125.68
123.71
122.49
113.59
74.18
64.71
59.21
57.34
42.33
36.42
30.55
28.61
26.97
26.00
25.46
22.60


CARBON01
smb-2-212f
f1 (ppm)
DIPP
Ru
i-Pr
19


CARBON01
smb-1-181
SI-28
Mes
Br
f1 (ppm)
13.10
18.09
21.32
29.78
35.43
41.72
63.84
126.50
129.08
129.17
129.93
135.03
135.22
141.10


CARBON01
smb-2-81
f1 (ppm)
SI-29
Mes
Ru
Cl
i-Pr
9.12
14.86
18.69
21.20
22.63
36.38
41.62
61.01
74.25
113.62
122.63
122.87
126.64
128.59
129.42
129.50
129.62
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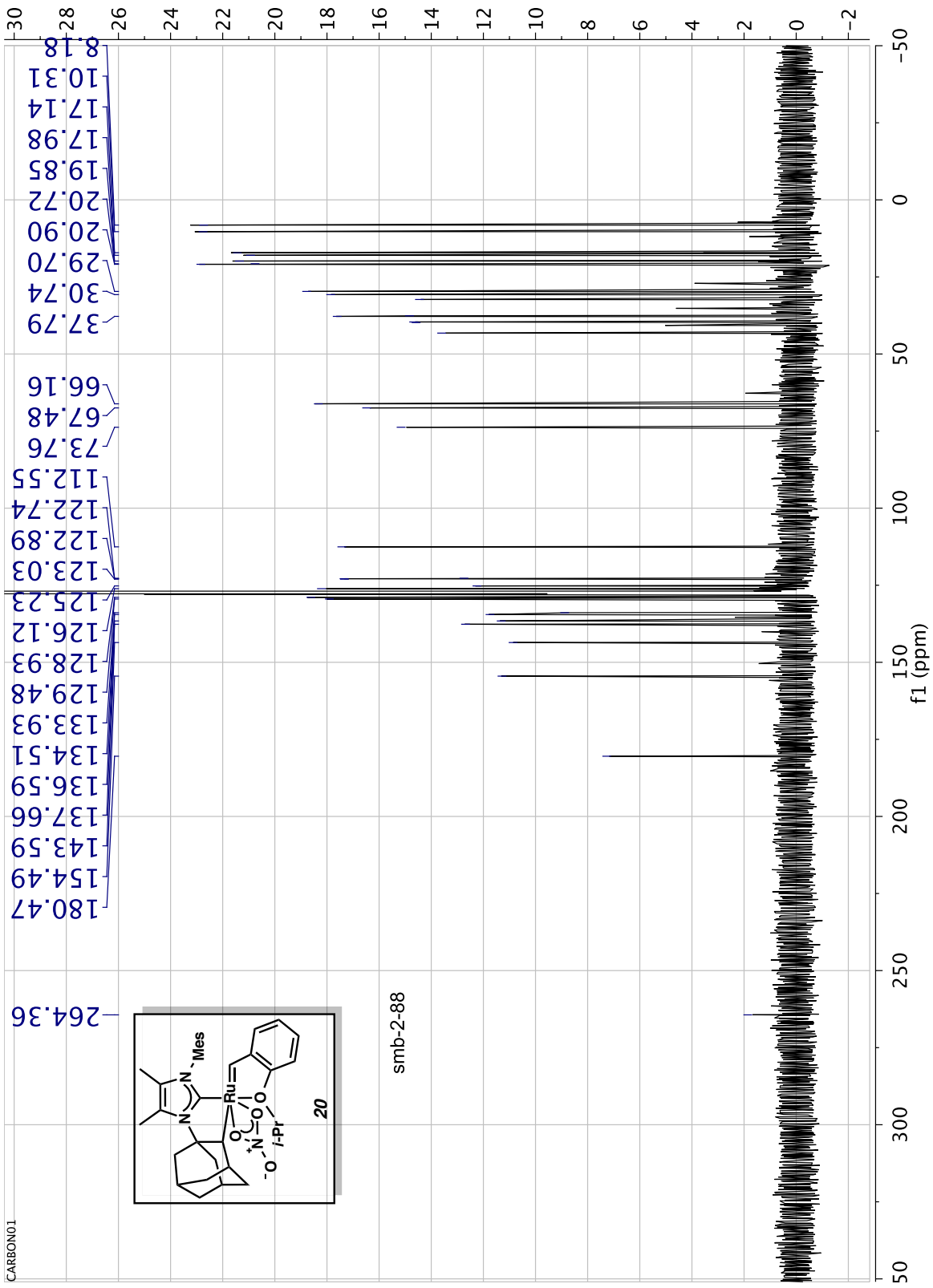
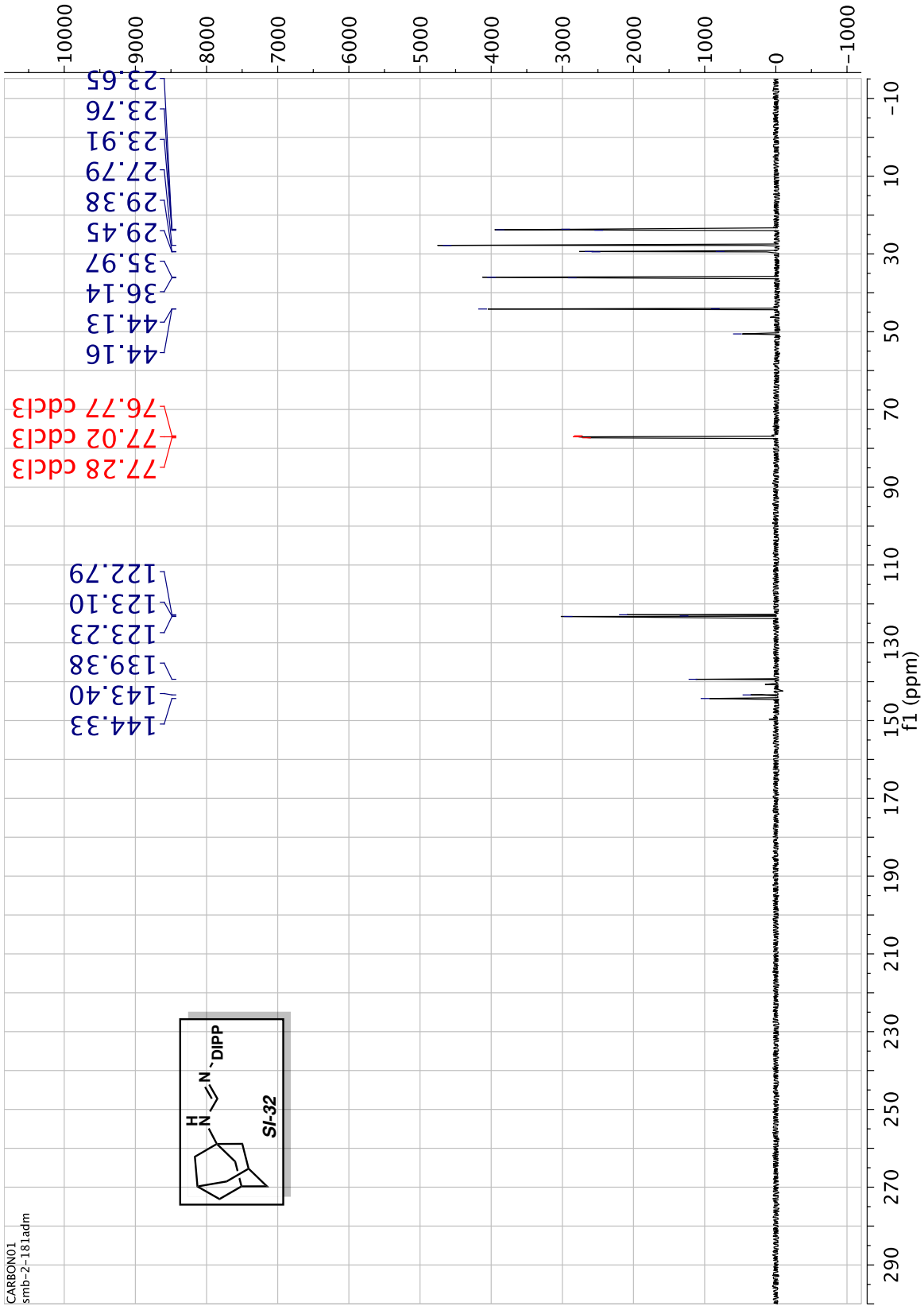
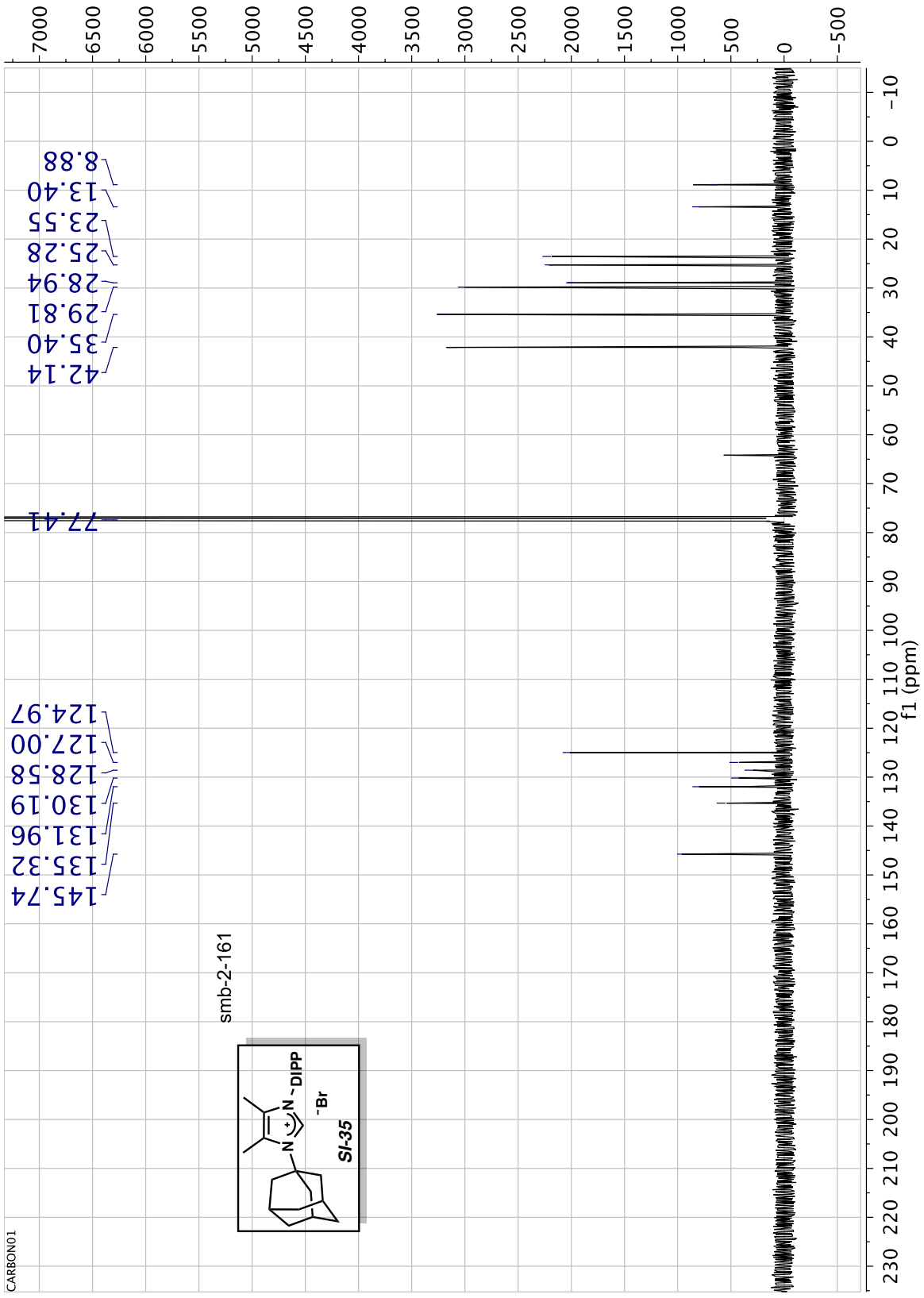
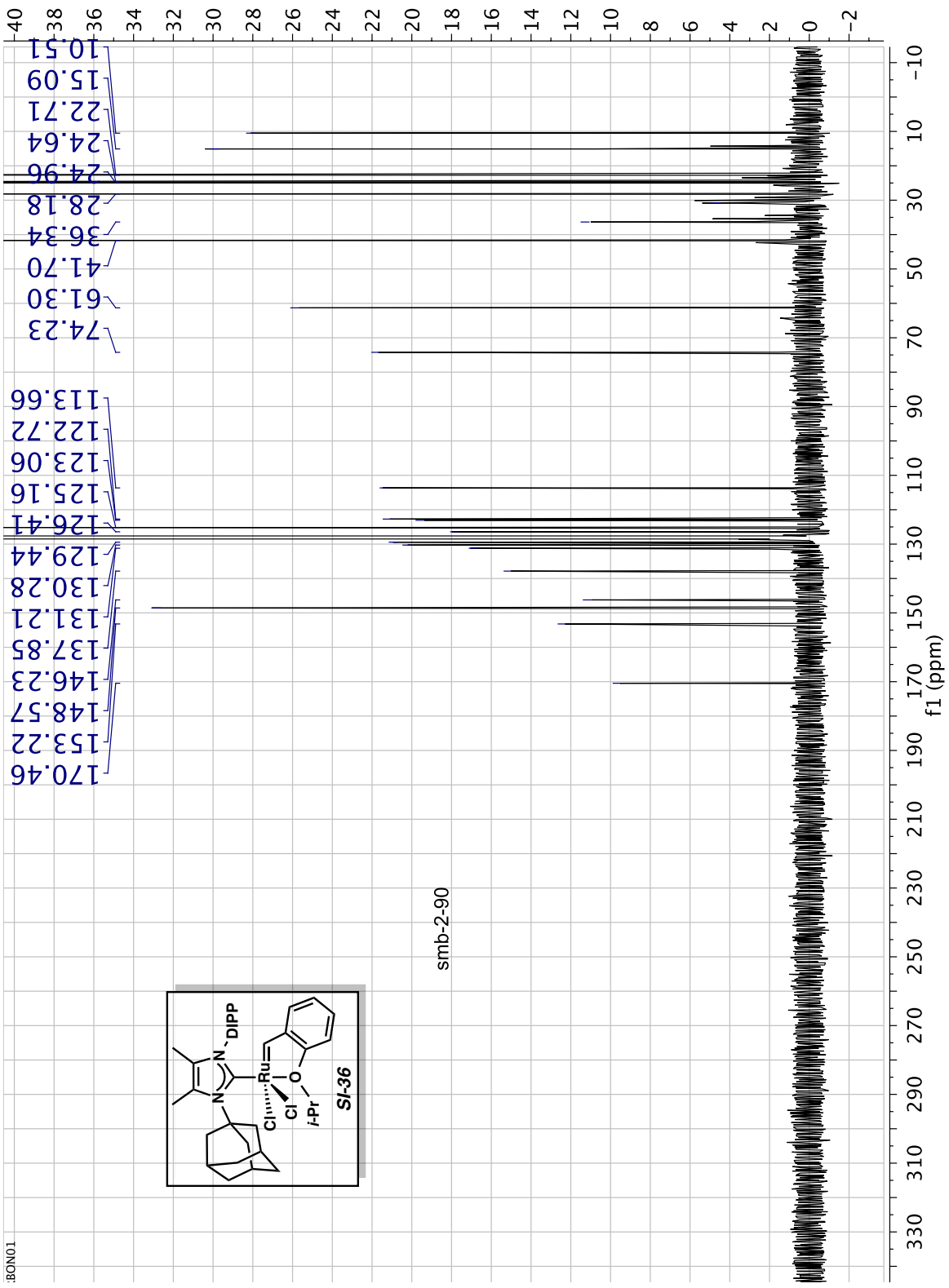
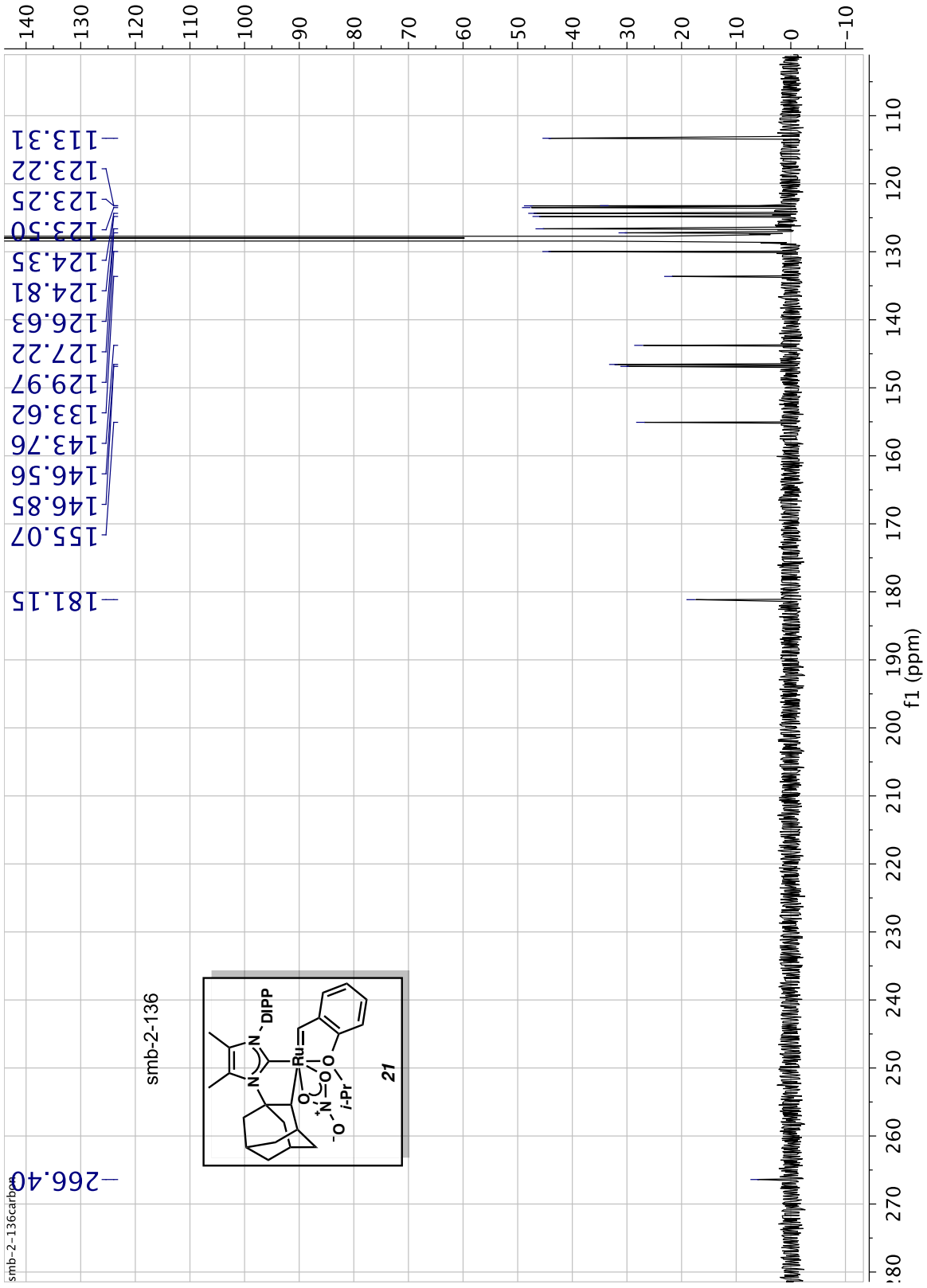
138.46
139.11
147.15
152.85
169.68
217.81
308.25

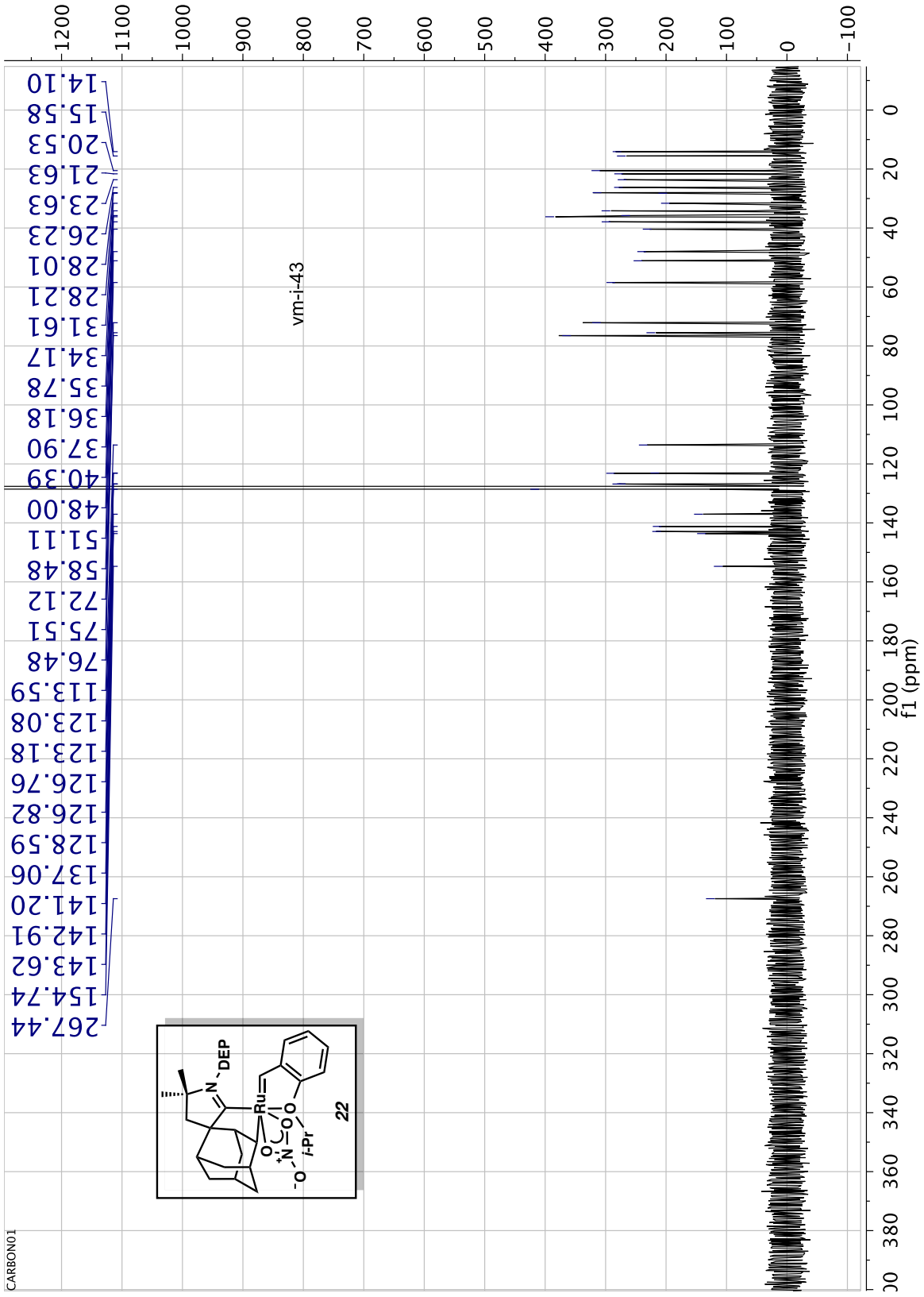

CARBON01
smb-2-88
20
Mes
i-Pr
Ru
f1 (ppm)
264.36
180.47
154.49
143.59
137.66
136.59
134.51
133.93
129.48
128.93
126.12
125.23
123.03
122.89
122.74
112.55
73.76
67.48
66.16
37.79
30.74
29.70
20.90
20.72
19.85
17.98
17.14
10.31
8.18

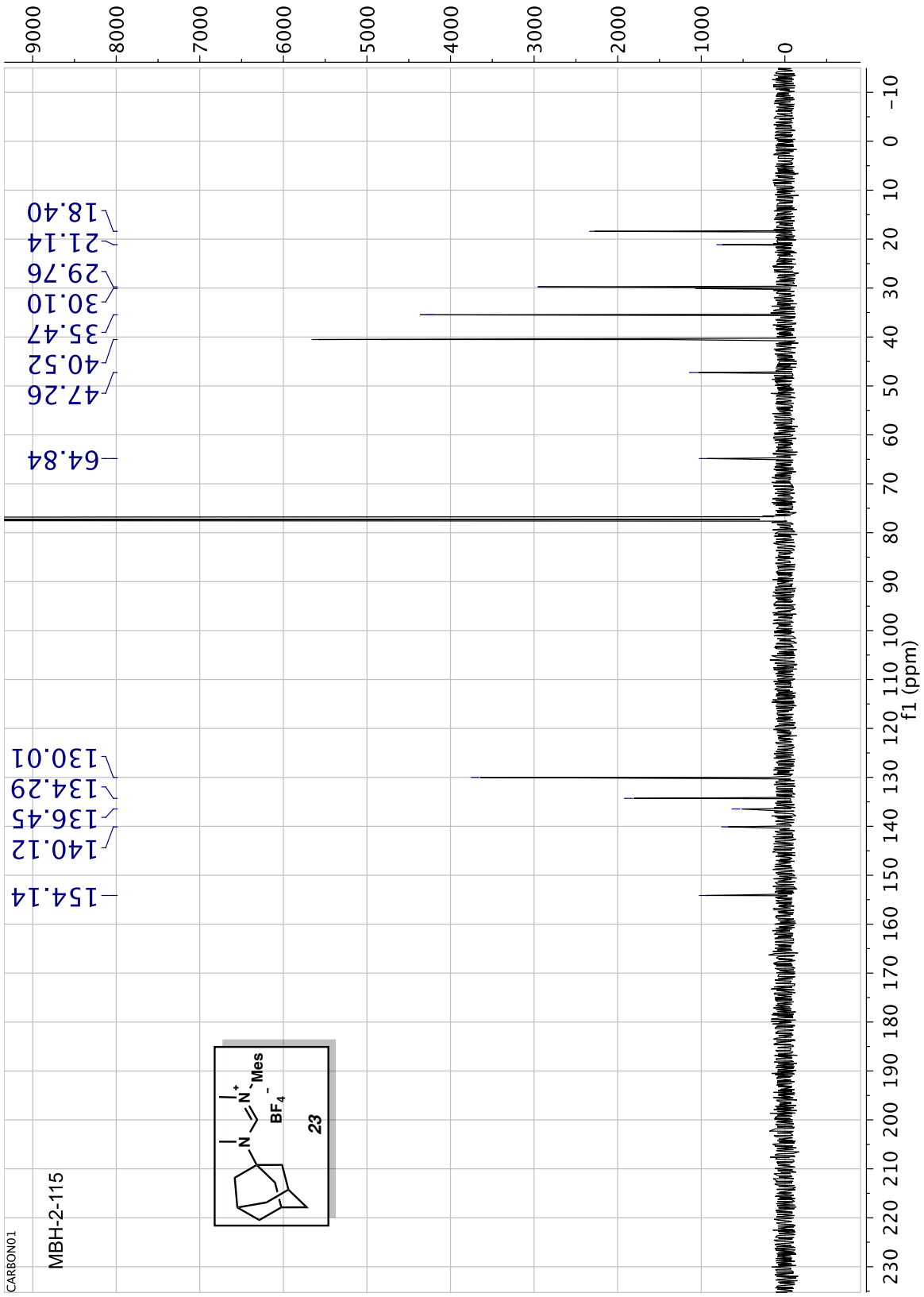

CARBON01
smb-2-181adm
SI-32
DIPP
144.33
143.40
139.38
123.23
123.10
122.79
77.28 cdcl3
77.02 cdcl3
76.77 cdcl3
44.16
44.13
36.14
35.97
29.45
29.38
27.79
23.91
23.76
23.65
f1 (ppm)

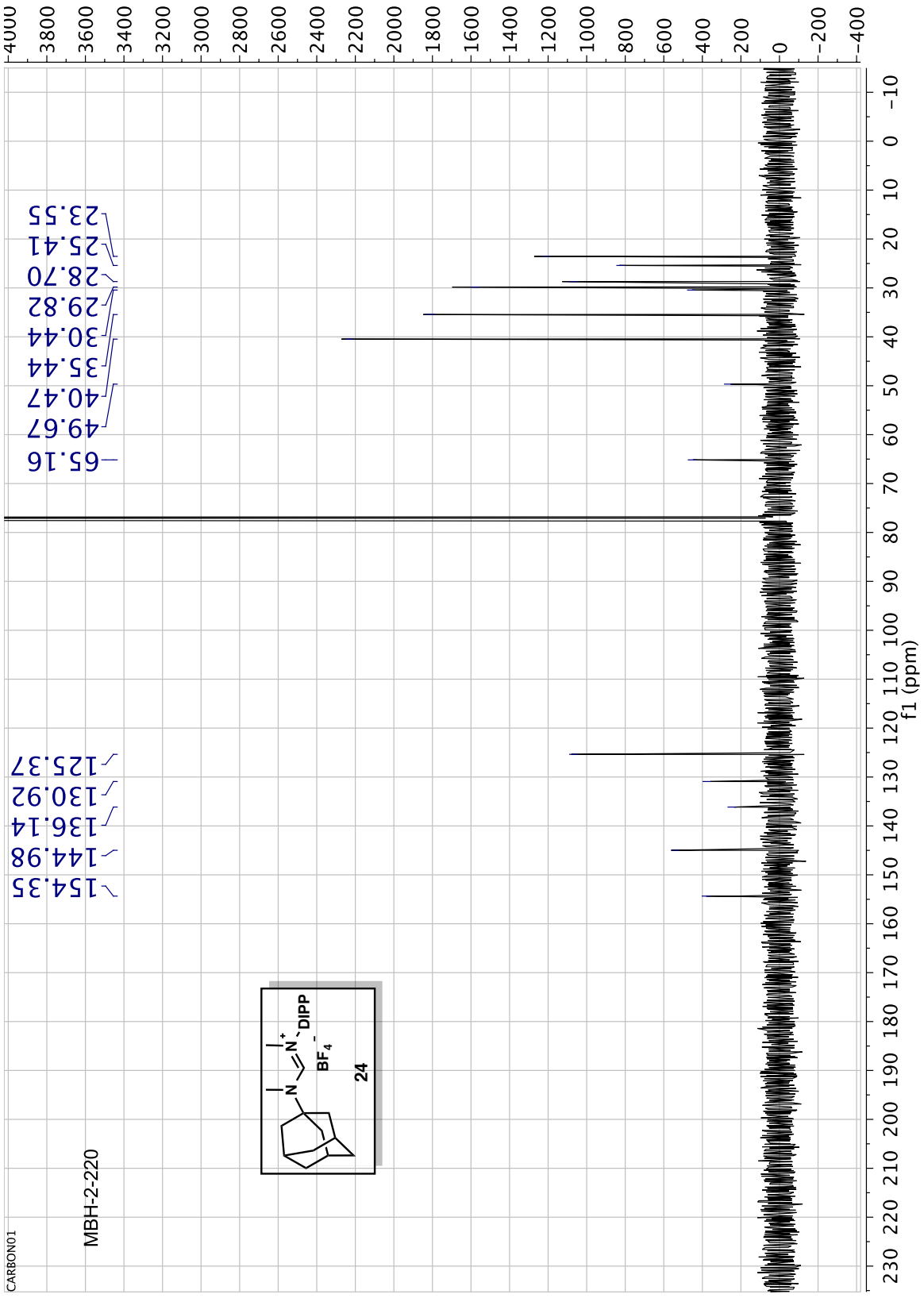

CARBON01
smb-2-161
SI-35
DIPP
Br
145.74
135.32
131.96
130.19
128.58
127.00
124.97
77.41
42.14
35.40
29.81
28.94
25.28
23.55
13.40
8.88
f1 (ppm)

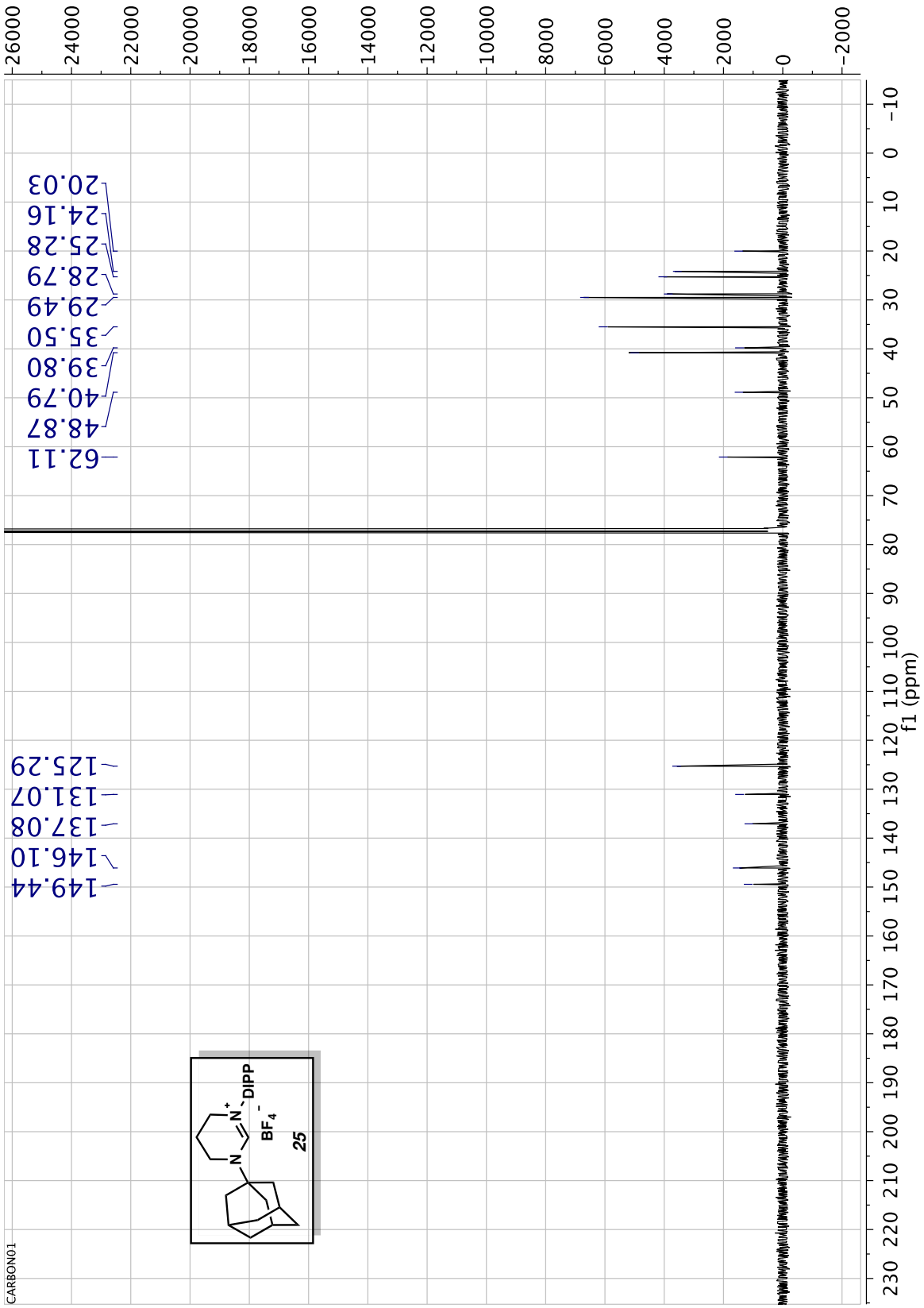

10.51
15.09
22.71
24.64
24.96
28.18
36.34
41.70
61.30
74.23
113.66
122.72
123.06
125.16
126.41
129.44
130.28
131.21
137.85
146.23
148.57
153.22
170.46
smb-2-90
DIPP
Ru
Cl
O
i-Pr
SI-36
f1 (ppm)

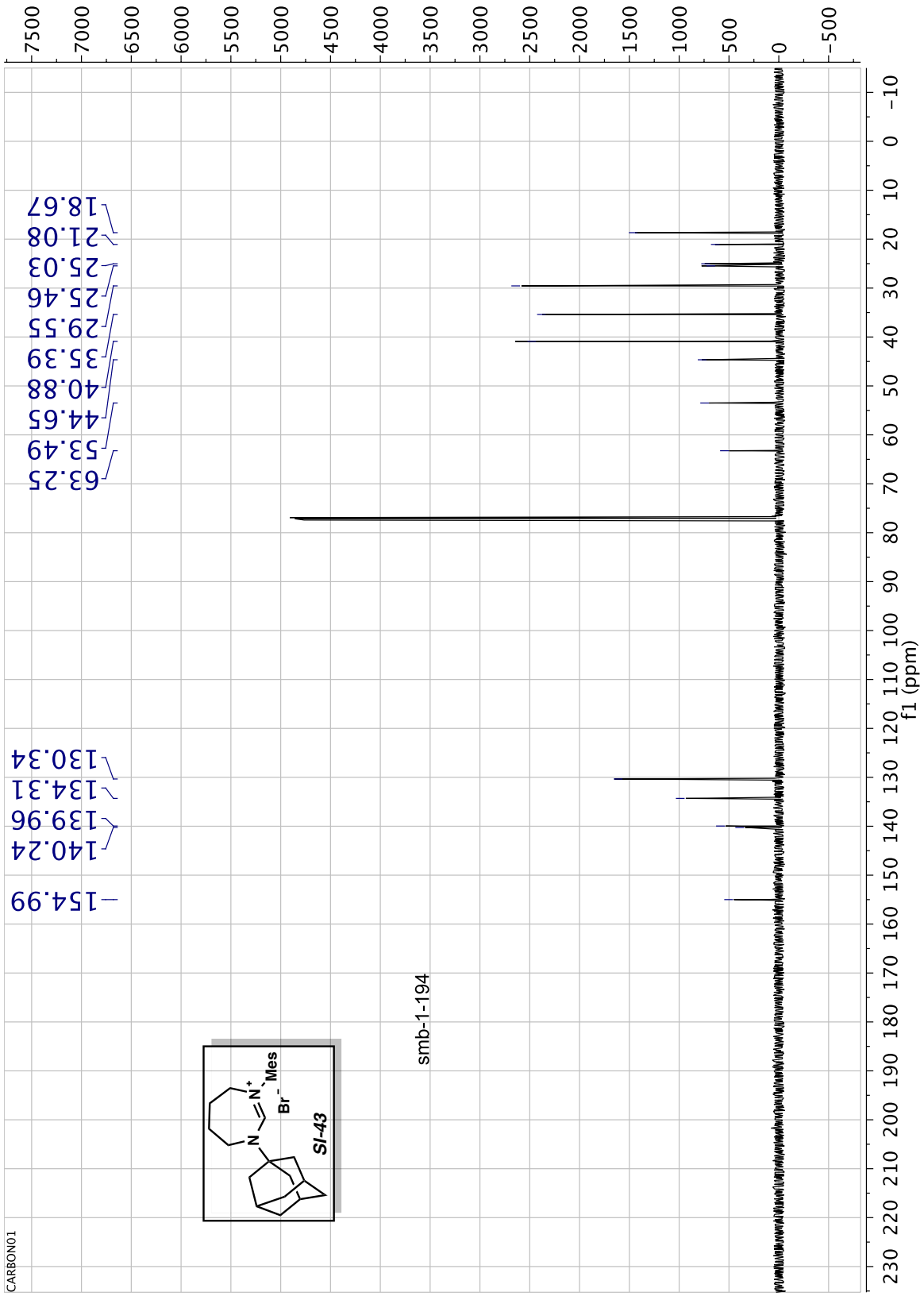

smb-2-136carbon
smb-2-136
DIPP
Ru
i-Pr
21
f1 (ppm)
266.40
181.15
155.07
146.85
146.56
143.76
133.62
129.97
127.22
126.63
124.81
124.35
123.50
123.25
123.22
113.31

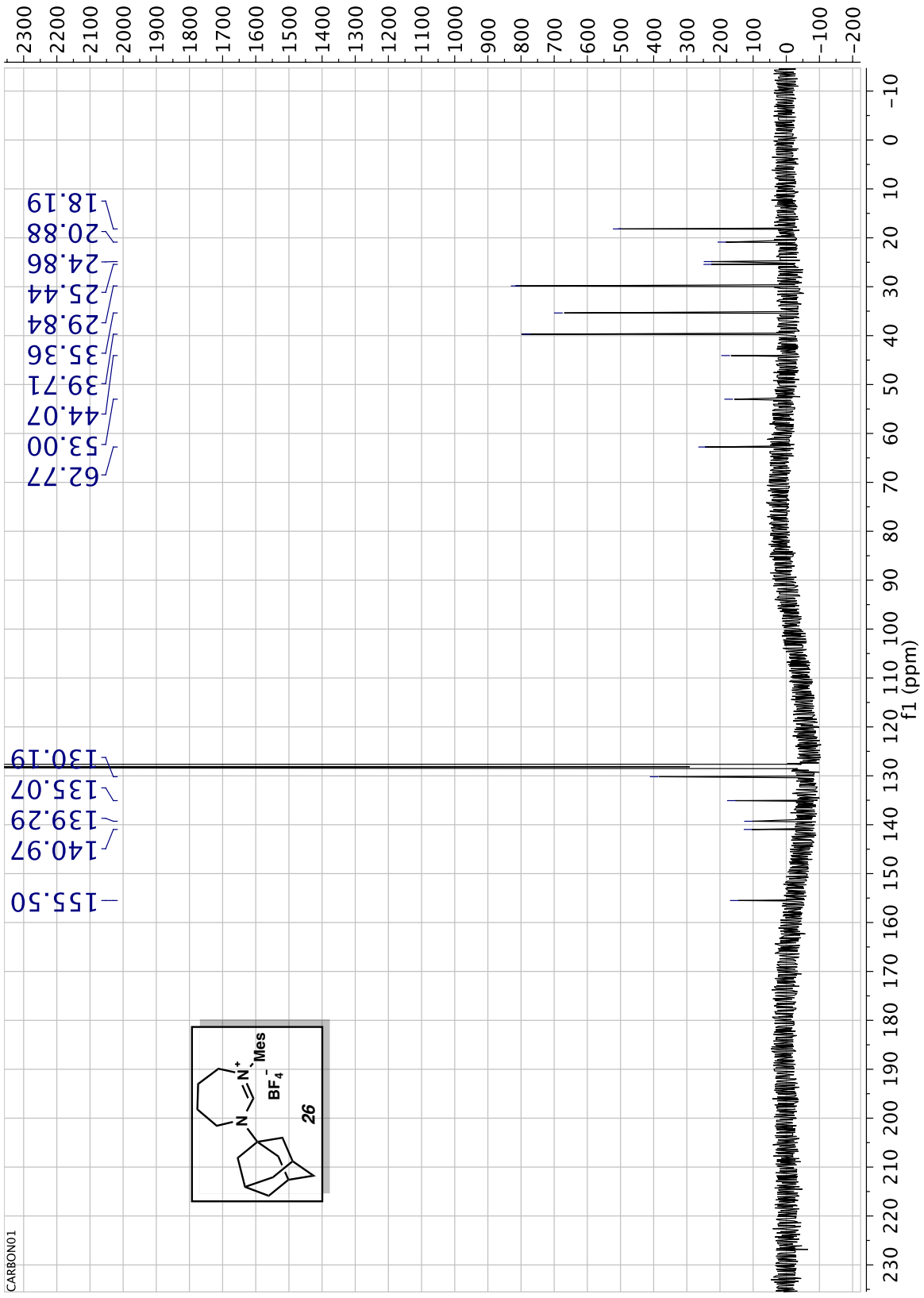

CARBON01
vm-i-43
f1 (ppm)
14.10
15.58
20.53
21.63
23.63
26.23
28.01
28.21
31.61
34.17
35.78
36.18
37.90
40.39
48.00
51.11
58.48
72.12
75.51
76.48
113.59
123.08
123.18
126.76
126.82
128.59
137.06
141.20
142.91
143.62
154.74
267.44
DEP
Ru
i-Pr
22

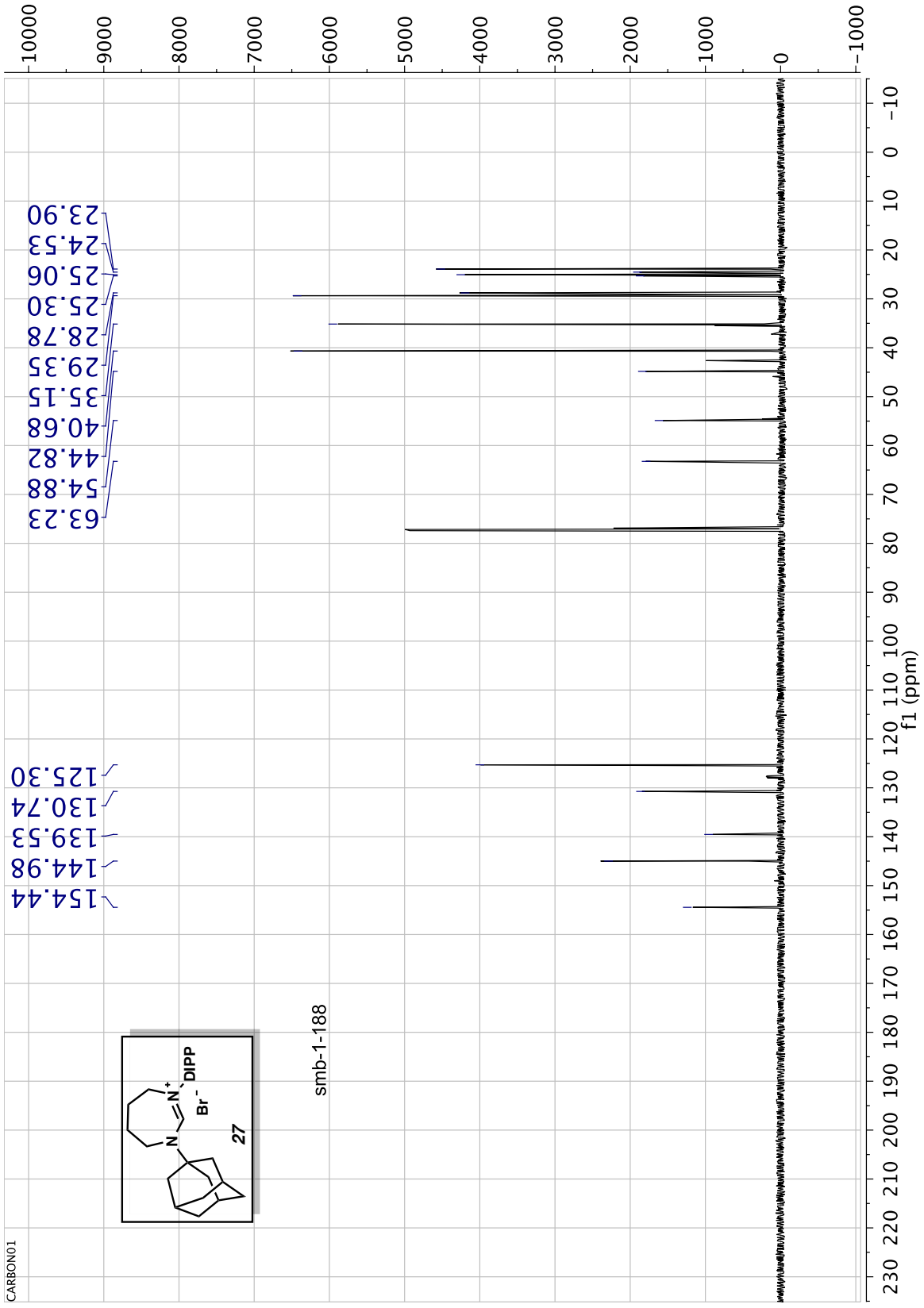

CARBON01
MBH-2-115
23
Mes
BF4
18.40
21.14
29.76
30.10
35.47
40.52
47.26
64.84
130.01
134.29
136.45
140.12
154.14
f1 (ppm)


CARBON01
MBH-2-220
24
DIPP
BF_4^-
154.35
144.98
136.14
130.92
125.37
65.16
49.67
40.47
35.44
30.44
29.82
28.70
25.41
23.55
f1 (ppm)


CARBON01
DIPP
BF4 -
25
20.03
24.16
25.28
28.79
29.49
35.50
39.80
40.79
48.87
62.11
125.29
131.07
137.08
146.10
149.44
f1 (ppm)


CARBON01
smb-1-194
SI-43
Mes
Br
N
f1 (ppm)
154.99
140.24
139.96
134.31
130.34
63.25
53.49
44.65
40.88
35.39
29.55
25.46
25.03
21.08
18.67


CARBON01
f1 (ppm)
18.19
20.88
24.86
25.44
29.84
35.36
39.71
44.07
53.00
62.77
130.19
135.07
139.29
140.97
155.50
Mes
BF4
26


CARBON01
smb-1-188
27
DIPP
Br⁻
f1 (ppm)
154.44
144.98
139.53
130.74
125.30
63.23
54.88
44.82
40.68
35.15
29.35
28.78
25.30
25.06
24.53
23.90

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6 For the synthesis of formamidine **SI-2**, see page SI-3.

7 The silica plug was found to be necessary in order to avoid substantial decomposition during C–H activation.

8 The synthesis, characterization and activity of compound **SI-39** are described in more detail in a pending publication. V. M. Marx, A. S. Sullivan, M. Melaimi, S. Virgil, D. Weinberger, G. Bertrand, R. H. Grubbs, *Manuscript in Preparation*.

9 For the synthesis of formamidine **SI-32**, see pages SI-21 and SI-22.

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